1-1-1970

Kinetics of sulfonation of dodecylbenzene by sulfur-trioxide.

Madhu Panchmia
University of Windsor

KINETICS OF
SULFONATION OF DODECYLBENZENE
BY SULFUR-TRIOXIDE

A Thesis
Submitted to the Faculty of Graduate Studies through the
Department of Chemical Engineering in Partial Fulfilment
of the Requirements for the Degree of
Master of Applied Science at the
University of Windsor

by

Madhu Panchmia

Windsor, Ontario
1970

ABH 9242

APPROVED BY: M B Powley

297777

ABSTRACT

Rate of reaction data for sulfonation of dodecylbenzene by sulfur-trioxide in 1,2-dichloroethane solution was obtained at 29°C. Sulfur-trioxide concentration in 1,2-dichloroethane was varied from 0.037 gm.moles/litre to 0.0653 gm.moles/litre. Dodecylbenzene concentration in 1,2-dichloroethane was varied from 0.08 gm.moles/litre to 0.12 gm.moles/litre. The reaction was rapid and complex. The kinetics were studied by obtaining the initial rate of the reaction. The results were:

$$-dC_i/dT = 5.325\ C_{H_i}^{0.563}\ C_{S_i}^{1.785}$$

where, C_{H_i} = initial concentration of dodecylbenzene in 1,2-dichloroethane, gm.moles/litre

C_{S_i} = initial concentration of sulfur-trioxide in 1,2-dichloroethane, gm.moles/litre

Short reaction times varying from 10 secs to 50 secs were taken and batch process was used.

ACKNOWLEDGMENTS

The auther takes this opportunity to express her sincere gratitude to Prof. M.B.Powley for his able guidance, constructive criticism and encouragement throughout this work and to Dr. Holland and Dr. Lam of Chemistry Department for their valuable suggestions from time to time.

The author is also very thankful to Mr. D.Hill of the Chemistry Department for determining the Infrared and the Nuclear Magnetic Resonance spectra, Mr. W.Eberhart and Mr.H. Eberhart for assistance in the construction of the experimental apparatus and Mr. G.Ryan for his valuable help at times on the apparatus.

M/S Continental Oil Company of U.S.A. supplied the Dodecylbenzene sulfonic acid free of cost for experimental purposes. The financial support for this work was provided by the National Research Council of Canada.

CONTENTS

FIGURES

TABLES

I. INTRODUCTION

Sulfonation of a compound gives sulfonic acid of that compound. Sulfonic acids are used as intermediates for production of many substances depending upon the initial compound used, e.g. surface active agents, dyes, pharmaceuticals, detergents, wetting and emulsifying agents, as acids in leather treatment, adhesives, aqueous thickeners etc.

Sulfonic acids are hardly ever used as such but they are used as intermediates in many industries. Yet, very little fundamental work has been done on sulfonation reactions. The optimum conditions for most commercial sulfonations are found by trial and error. Demand for all these products has increased tremendously after World War II. For instance, in the case of surface active agents the demand has increased almost tenfold during the years 1943-1953(Table 1)(1).

The demand for detergents has been increasing rapidly since then. Dodecylbenzene is by far the most common starting material used in detergent industry, even though aliphatic compounds are also being used these days.

Purpose of this experiment is to study the kinetics of the sulfonation of dodecylbenzene by sulfur-trioxide. The rate equation can generally be written as:

$$- dC/dT = k\, C_H^{\alpha} C_S^{\beta} \quad \text{.....(1)}$$

TABLE 1

Production of Organic Surface Active Agents

(Units in 1000 lbs)

Year	Petroleum based	Other	Total
1943	51,538	48,445	99,983
1944	74,234	78,402	152,636
1945	79,004	105,434	184,442
1946	99,813	142,361	242,174
1947	112,687	174,474	291,161
1948	177,737	196,978	374,715
1949	232,721	196,635	429,356
1950	371,602	286,268	657,870
1951	502,567	186,337	688,904
1952	546,774	189,627	736,401
1953	711,620	203,093	914,713

The unknowns α, β and k are found experimentally,

where k = velocity constant of the reaction

α = order of reaction with respect to hydrocarbon, which is dodecylbenzene

β = order of reaction with respect to sulfur-trioxide

C_H = concentration of dodecylbenzene in the solvent

C_S = concentration of sulfur-trioxide in the solvent

II. LITERATURE SURVEY

Kinetic study of the sulfonation of aromatic hydrocarbon by sulfuric acid and oleum has been done before. But, kinetic study of sulfonation by sulfur-trioxide has not been very common. Vicary and Hinshelwood in 1939 first published a paper on their studies of sulfonation of nitrobenzene by sulfur-trioxide (2). Nitrobenzene is itself used as a solvent. The reaction was stopped and products were analysed by extraction with water and benzene. The unchanged nitrobenzene went into the benzene layer and the acids into the aqueous layer. The benzene layer was washed with water, the washings added to the aqueous layer and the whole titrated. This solution was boiled down to 100 c.c. and analysed for sulfuric acid by gravimetric determination as barium sulfate.

Tests were made for sulfone formation. It was found to be negligible. Also, the reaction was found to be of second order with respect to sulfur-trioxide, little influenced by sulfuric acid at higher temperature, retarded by it at lower temperatures and strongly retarded by the formation of addition compound between sulfuric acid and sulfonic acid.

Again, in 1944, Wadsworth and Hinshelwood in continuation of their kinetic investigation studied the

sulfonation of p-nitrotoluene and chlorobenzene by sulfur-trioxide (3). Both the reactions show characteristics similar to those found in sulfonation of nitrobenzene, being of second order with respect to sulfur-trioxide and exhibiting strong retardation due to formation of complex between sulfur-trioxide and sulfonic acid.

The second order of the reaction with sulfur-trioxide shows that it must proceed by a mechanism involving either (a) S_2O_6 molecule in equilibrium with small amount of SO_3 molecules,or (b) two SO_3 molecules. It was not known whether the dimer was in fact present to any appreciable extent in dilute solutions in nitrobenzene (solvent in these cases) though Michael and Weiner (4) present evidence of certain preparative reactions indicating that S_2O_6 is the active agent in sulfonation. If the mechanism involved two trioxide molecules, the second molecule might (i) enter into some relation with the nitrogroup which enhances the activity of benzene nucleus, or (ii) act in a manner analogous to a basic catalyst, by providing a temporary home for proton replaced from the C-H bond by the first trioxide molecule. Further study of aromatic compounds was found to be necessary to resolve all the various possibilities.

In this case, since sulfonation of chlorobenzene, like that of nitro-compounds, depends on the second power of sulfur-trioxide concentration, it follows that the second order reaction does not arise from a specific

property of the nitrogroup. It might, however, depend on a property of all strongly polar substituent group. Therefore, detailed mechanism was unsolved until data for benzene or derivatives had been obtained. In any case, under the conditions prevailing of S_2O_6 as the active species, the scheme

$$2\ SO_3 \rightleftharpoons S_2O_6 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

$$ArH + S_2O_6 \longrightarrow Ar.S_2O_6.H \quad \ldots\ldots\ldots\ldots\ldots (3)$$

$$Ar.S_2O_6.H \longrightarrow ArSO_3H + SO_3 \quad \ldots\ldots\ldots\ldots (4)$$

is attractive since this explains both second order with respect to sulfur-trioxide and the retardation of the reaction as it proceed.

The same year Dresel and Hinshelwood (5) published another paper on sulfonation of benzene, bromobenzene, m-dichlorobenzene, α-nitronapthalene and p-nitroanisole. All reactions are found to be second order with respect to sulfur-trioxide and to exhibit the characteristic retardation by the product. The first order with respect to aromatic reactant which had been anticipated was confirmed experimentally. From this information the mechanism of substitution by sulfur-trioxide can be conclusively said to be:

$$2\ SO_3 \rightleftharpoons S_2O_6 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (5)$$

$$ArH + S_2O_6 \longrightarrow Ar.S_2O_6.H \quad \ldots\ldots\ldots\ldots\ldots (6)$$

$$Ar.S_2O_6.H \longrightarrow ArSO_3H + SO_3 \quad \ldots\ldots\ldots\ldots (7)$$

Leierson, Bost and LeBaron (6) studied benzene sufonation in liquid sulfur-dioxide and attributed

sulfone formation to three factors:

(a) Order of addition of benzene and sulfur-trioxide to liquid sulfur-dioxide,

(b) the warming of the reaction mixture after mixing of the reactants from -8°C to room temperature with accompanying expulsion of sulfur-dioxide, and

(c) the purity of benzene. But, it was found later that extent of sulfone formation was dependant chiefly on the temperature (Fig. 1) of the reaction and specially on the mole ratio of benzene to sulfur-trioxide at various stages of synthesis.

As seen above, sulfonation is a very rapid process for accurate kinetic measurements by conventional methods. This difficulty was overcome by Ratcliffe (7) by using sulfur-trioxide in a less reactive form and by using continuous flow method. The rate of reaction of benzene by sulfur-trioxide in 1,2-dichloroethane was found to be:

$$- dC_i/dT = 5.11\ C_{Hi}^{0.57}\ C_{Si}^{1.24} \quad \text{.....(8)}$$

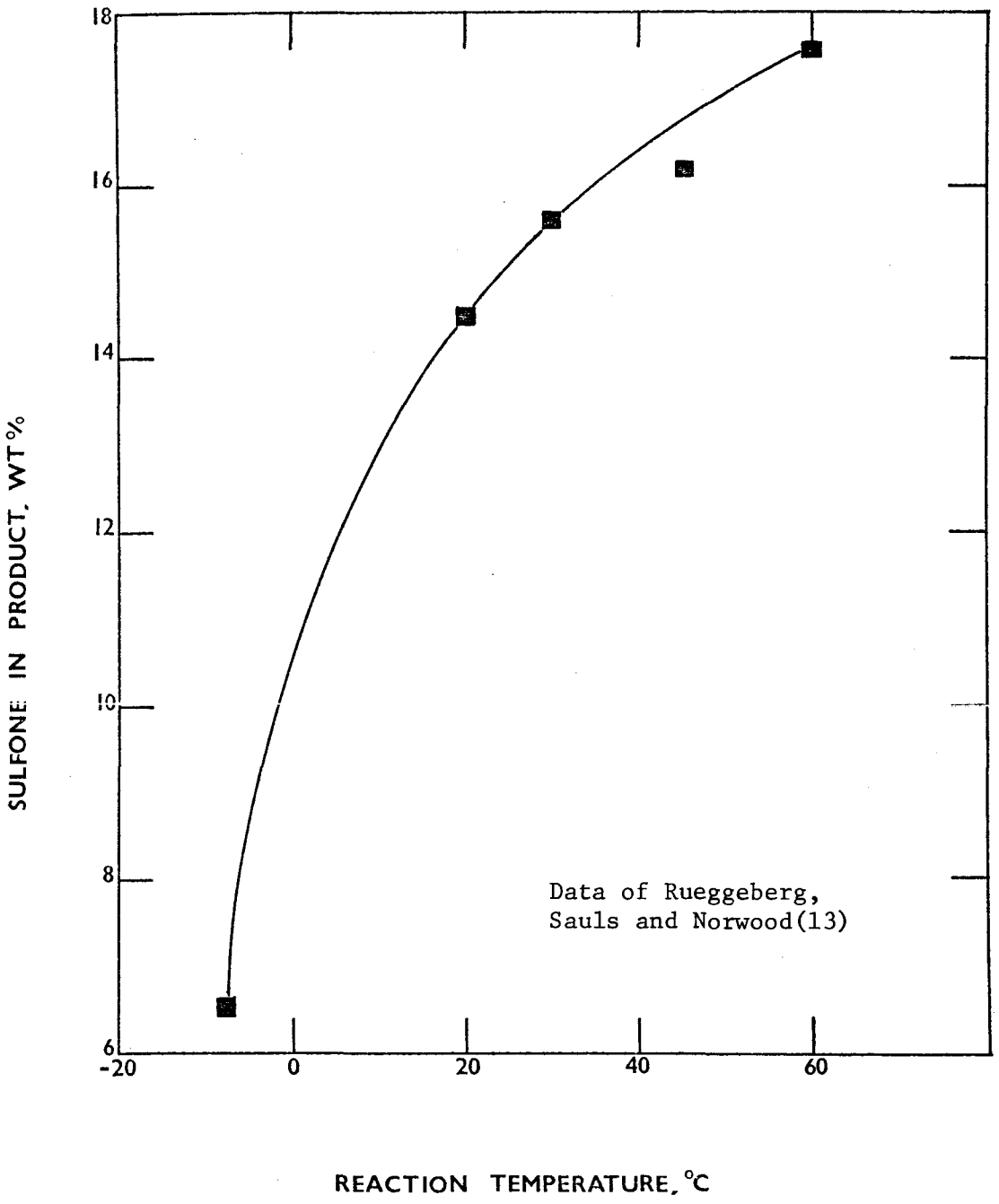


FIG. 1 SULFONE FORMATION AS A FUNCTION OF TEMPERATURE

III. THEORY

A. SULFONATION

Sulfonation may be defined as addition of sulfonic acid group ($-SO_3H$) to a carbon atom of an organic compound.

There are two types of sulfonation reactions:

(a) Indirect

and (b) Direct

Sulfonic acid salt is prepared by indirect sulfonation. This is the desired product in industry for manufacture of detergents. For example,

$$RCl + Na_2SO_3 \longrightarrow RSO_3Na + NaCl \quad \ldots\ldots\ldots\ldots\ldots (9)$$

Many sulfonic acids, specially, aromatic sulfonic acids may be prepared by direct sulfonation.

(a) Sulfuric acid

(b) Oleum

(c) Sulfur-trioxide-liquid or vapor

(d) Addition compound of sulfur-trioxide

(e) Chlorosulfonic acid

(f) Sulfur-trioxide in a solvent

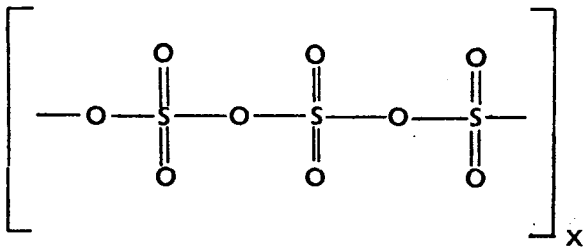
(g) Sulfur-dioxide and oxygen or sulfur-dioxide and chlorine

(h) Sulfites, sulfates etc.

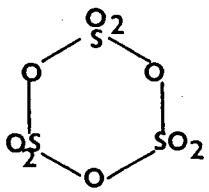
Which sulfonating agent is to be used depends on the physical properties of the compound to be sulfonated. For almost all types of aromatic hydrocarbons, sulfuric acid and oleum are by far the most common commercial sulfonating agents. These can be thought of as compounds

of sulfur-trioxide with ease of release to the organic material being sulfonated varying from one reagent to another.

Even though sulfur-trioxide seems to be the best direct sulfonating agent, for many years use of sulfur-trioxide on a commercial scale was limited to manufacturers. This was due to the instability of sulfur-trioxide in its γ-form, which is liquid at ordinary temperature. It has a tendency to polymerize to straight chain β-polymer and cross-linked α-polymer.



.....β-polymer



..... α-polymer

Therefore, until recent years its use had been limited to manufacturers who had been able to take advantage of their own contact acid plants or who had been prepared to obtain it by distillation from oleum.

After considerable research Allied Chemical & Dye Corporation of U.S.A. (8) overcame the difficulties associated with liquid sulfur-trioxide and introduced their stable γ-product "Sulfan". Stabilization is achieved

by adding 0.1% of various compounds- derivatives of boron, phosphorus and sulfur. It has approximately 99.5% active sulfur-trioxide content. Sulfan was first offered commercially in 1950. It had been so much in demand since then that the company erected its second production plant by 1956. In England, Hardman & Holden Ltd. arranged to manufacture Sulfan under licence from Allied Chemical & Dye Corporation. Bulk supplies were available in England by 1957.

Sulfan has greatly increased production of some industrial sulfonates- surface active agents, lubricants, additives, aqueous thickeners, synthetic gums and ion exchange resins.

Some of the physical properties of γ-sulfur-trioxide are given below.

TABLE 2

Physical Properties of γ-Sulfur-trioxide

Boiling Point	44.8 ^{o}C
Melting Point	16.8 ^{o}C
Specific Gravity(20-30^{o}C)	1.9224-1.88
Specific Heat(25-35^{o}C)	0.77cal/gm
Heat of Dilution	504 cal/gm
Heat of Vaporization	127.4 cal/gm
Viscosity at 30^{o}C	1.524 cp

Sulfur-trioxide is different from sulfuric acid in that it is miscible in all proportions in liquid sulfur-dioxide and in many chlorinated and fluorinated organic solvents. Some of the solvents react with sulfur-trioxide depending on the purity of the solvent and nature of the stabilizer.

Some of the advantages and disadvantages of sulfur-trioxide compared to sulfuric acid are given below:

Advantages:

(a) No water is produced during the reaction. The reaction is essentially

$$RH + SO_3 \longrightarrow RSO_3H \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

whereas, with sulfuric acid or oleum the reaction is

$$RH + H_2SO_4 \longrightarrow RSO_3H + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (11)$$

Sulfonation reaction ceases below a certain minimum sulfuric acid concentration. This was shown by Guyot(9). Courtot (10) and Spryskov (11) showed that this concentration, which was designated as π, depends for any particular reaction, on the nature of the compound, the extent to which sulfur-trioxide forms addition compound with sulfonic acid produced , the reaction temperature, the amount and concentration of sulfuric acid used and the time of reaction. Since sulfuric acid forms water, the acid concentration decreases and therefore,to maintain the π value so as not to let the reaction stop excess acid is required. In case of sulfur-trioxide no water is formed and therefore

no excess acid is required.

(b) As there is no excess acid present, no excess alkali is required while neutralization thus reducing the content of inorganic sulfates in the final product. This is particularly important when detergent is to be prepared from the sulfonic acid formed.

(c) Smaller equipment is required for the same output as volume of the acid is reduced. Besides, the faster reaction reduces the reaction time.

Disadvantages:

(a) Sulfur-trioxide is more difficult to handle than sulfuric acid and oleum.

(b) Heat of reaction is very high, so, more provision for cooling is necessary.

(c) The very rapid and highly exothermic reaction with liquid sulfur-trioxide frequently causes charring. So,for getting light colored products use of solvents is necessary.

A major object in choosing a suitable sulfonation reagent and process is the avoidance of side reactions, the nature and extent of which will depend upon the structure of the compound to be sulfonated, the sulfonating agent and physical conditions used. The principle side reactions encountered with aromatic compounds are sulfone formation, polysulfonate formation of undesired isomers and oxidation(12).

Formation of sulfone proceeds according to the reactions given below:

$$RH + SO_3 \longrightarrow RSO_3H \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (12)$$

$$RH + RSO_3H \longrightarrow R_2SO_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (13)$$

Overall reaction:

$$2\ RH + SO_3 \longrightarrow R_2SO_2 + H_2O \quad \ldots\ldots\ldots\ldots\ldots\ldots (14)$$

Factors favoring sulfone formation:

(i) Use of strong reagent.

(ii) Operation in vapor rather than in liquid phase.

(iii) High reaction temperature (Fig. 1).

Factors favoring reduction of sulfone formation:

(i) Use of solvent.

(ii) Addition of organic compound to the sulfonating agent.

(iii) Conducting the reaction in comparitively large volume of reaction products.

(iv) Use of chemical inhibitors, for example, acetic acid (Fig. 2) (13).

(v) In benzene series increasing substitution by a number or length of alkyl group reduces sulfone formation.

Polysulfonation is specially pronounced in polycyclic compounds. Compounds such as anthracene and phenanthracene polysulfonate very easily. Preparation of monosulfonate involves a substantial amount of undesired polysulfonate even in presence of unreacted hydrocarbon. Benzene, napthalene and dodecylbenzene are easily sulfonated without substantial disulfonation.

Oxidation is another side reaction which is noted specially with polycyclic hydrocarbons and with poly-

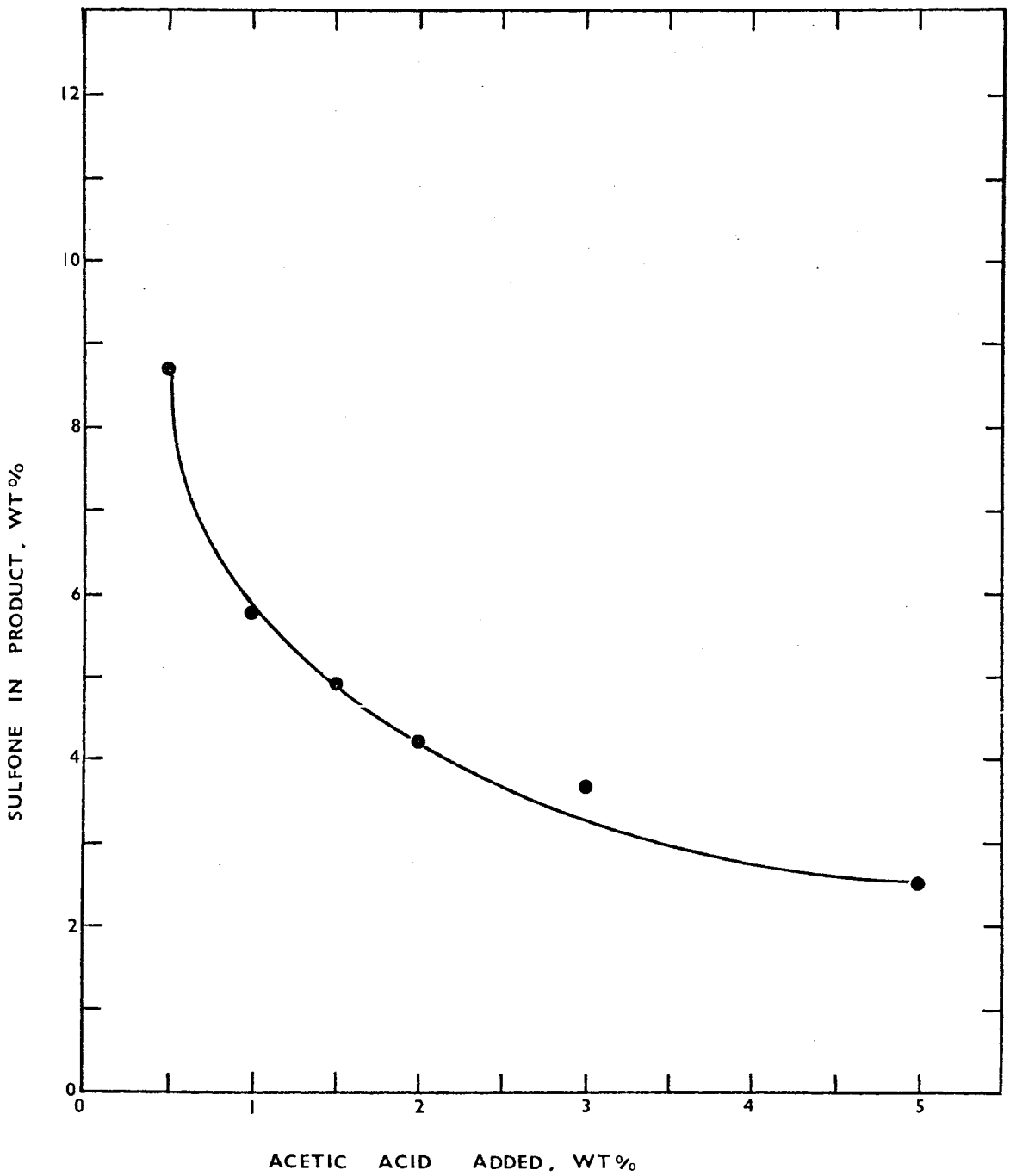


FIG. 2 EFFECT OF ACETIC ACID ON SULFONE FORMATION

alkylated benzene derivatives at elevated temperatures and in presence of catalytic material such as mercury.

B. REACTION KINETICS

The rate of chemical reaction may usually be expressed by the equation:

$$- dC/dT = kC_A^{\alpha} C_B^{\beta} \quad \text{.....(15)}$$

where $- dC/dT$ = rate of reaction

k = velocity constant

C_A, C_B = concentration of reactants in gm.moles/lit.

α, β = order of reaction with respect to the reactants A and B respectively

There are a number of methods used for finding orders and velocity constant.

(a) Integration method:

For n^{th} order reaction involving only one reactant, or where the initial concentrations of the reactants are equal and the reaction involves equal numbers of moles of each reactant:

$$- dC/dT = k.C^n \; ; \qquad - dC/C^n = k.dT$$

$$\text{or, } -\int_{C_o}^{C} dC/C^n = k\int_0^T dT$$

$$\text{or, } \frac{1}{(n-1)} \left(1/C^{n-1} - 1/C_o^{n-1} \right) = kT$$

$$\text{or, } k = \frac{1}{T\,(n-1)} \left(1/C^{n-1} - 1/C_o^{n-1} \right) \quad \text{.....(16)}$$

where, C_o = initial concentration

C = concentration at any time T

T = time

n = order of the reaction

Values of k are calculated for each value of T for several values of n. The value of n giving a constant value of k is the order of the reaction. This is misleading if applied to a complex reaction.

(b) Fractional period method:

A related method to the above is a fractional period method. The time T at which a definite fraction of the reaction is complete is measured. For n^{th} order reaction:

$$C = (1-x)C_o$$

$$\text{Then, } k = \frac{1}{T_x(n-1)}\left[\frac{1}{(1-x)^{n-1}C_o^{n-1}} - \frac{1}{C_o^{n-1}}\right]$$

$$\text{or, } T_x = \frac{1-(1-x)^{n-1}}{k(n-1)(1-x)^{n-1}}\,(1/C_o^{n-1})$$

$$\text{or, } T_x = \text{constant} \cdot (1/C_o^{n-1}) \quad \ldots\ldots\ldots\ldots\ldots\ldots (17)$$

The order n may be found by plotting logT against $\log C_o$. This method suffers from the same drawbacks as the method of integration.

(c) Isolation method:

This method is used only for reactions that are not

complex. A reaction has orders $\alpha, \beta, \gamma, \ldots\ldots$ with respect to reactants A,B,C, ... respectively. Now, if B and C are present in large excess, their concentration will not change appreciably during the course of the reaction. The apparent order of the reaction will then be α. β and γ are determined in a similar way.

(d) Differential method:

Differential method is applicable to complex reactions. For n^{th} order reaction involving only one reactant:

$$- dC/dT = k.C^n \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (18)$$

The rate (-dC/dT) is found by drawing tangents to a plot of concentration versus time. On plotting log(-dC/dT) against log(concentration), a simple reaction will give a straight line with slope the true order n. A complex reaction may give a straight line or a curve; the slope of the straight line may not correspond to the true order. If a straight line is obtained, the initial rate may be found by extrapolation. A plot of log(initial rate) against log (initial concentration) gives a straight line with the slope equal to the true order.

For two reactants, as in the present case, sulfur-trioxide and hydrocarbon dodecylbenzene,

$$- dC/dT = k\, C_H^{\alpha} C_S^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (19)$$

Concentration of sulfur-trioxide C_S in the solvent is kept constant. For a particular value of dodecylbenzene concentration C_H in the solvent a plot of $\log C_H$ versus time is obtained. C_H is varied and a number of such plots drawn.

Each plot is extrapolated to T=0 and a tangent drawn at these points. The tangent is ($-\ d\log C_i/dT$), which is,

$$-\ d\log C_i/dT = -\frac{1}{C_i}.\ (dC_i/dT) \quad \ldots\ldots\ldots\ldots\ldots\ldots (20)$$

From equation (20) the initial rate ($-dC_i/dT$) is calculated and a plot of log (initial rate) versus log (initial concentration) is drawn. The straight line gives:

$$-\ dC_i/dT = k_1 . C_{H_i}^{\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (21)$$

where, $k_1 = k . C_{S_i}^{\beta}$ .....(22)

Similarly by keeping C_H constant,

$$-\ dC_i/dT = k_2 . C_{S_i}^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (23)$$

where, $k_2 = k . C_{H_i}^{\alpha}$ .....(24)

Value of k can be calculated from the above equations (22) and (24) to give the final equation

$$-\ dC_i/dT = k\ C_{H_i}^{\alpha}\ C_{S_i}^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots (25)$$

where, C_{H_i} = initial hydrocarbon concentration

C_{S_i} = initial sulfur-trioxide concentration

IV. EXPERIMENTAL

Dodecylbenzene is sulfonated by sulfur-trioxide in 1,2-dichloroethane solution.

A. EQUIPMENT & PROCEDURE

Sulfur-trioxide is dissolved in 1,2-dichloroethane by passing sulfur-trioxide diluted with air through 1,2-dichloroethane (Fig. 3). This dissolution process is carried out under a fume-hood. Air is passed through a U-tube which contains cotton for removing any oil or grease and then through another U-tube containing "6-16 mesh Grade 05" silica gel for removing moisture from the air. A small amount of indicating silica gel is put in the U-tube so as to get an indication of when the silica gel is incapable of absorbing any moisture.

This purified air is passed through a 1000 c.c. round bottom flask containing "Sulfan". Sulfan has a tendency to to solidify at room temperature, therefore the sulfan flask is heated by a bunsen burner. The air passing through the sulfan flask evaporates it to sulfur-trioxide and carries it to a bottle containing 1,2-dichloroethane. Sulfur-trioxide is dissolved in 1,2-dichloroethane. Air and the remaining sulfur-trioxide is let out in the fume-hood.

Since dodecylbenzene is liquid at room temperature, there is no elaborate equipment necessary for forming the solution . Necessary amount of dodecylbenzene is added to 1,2-dichloroethane and stirred.

After the solutions are prepared strong sulfur-

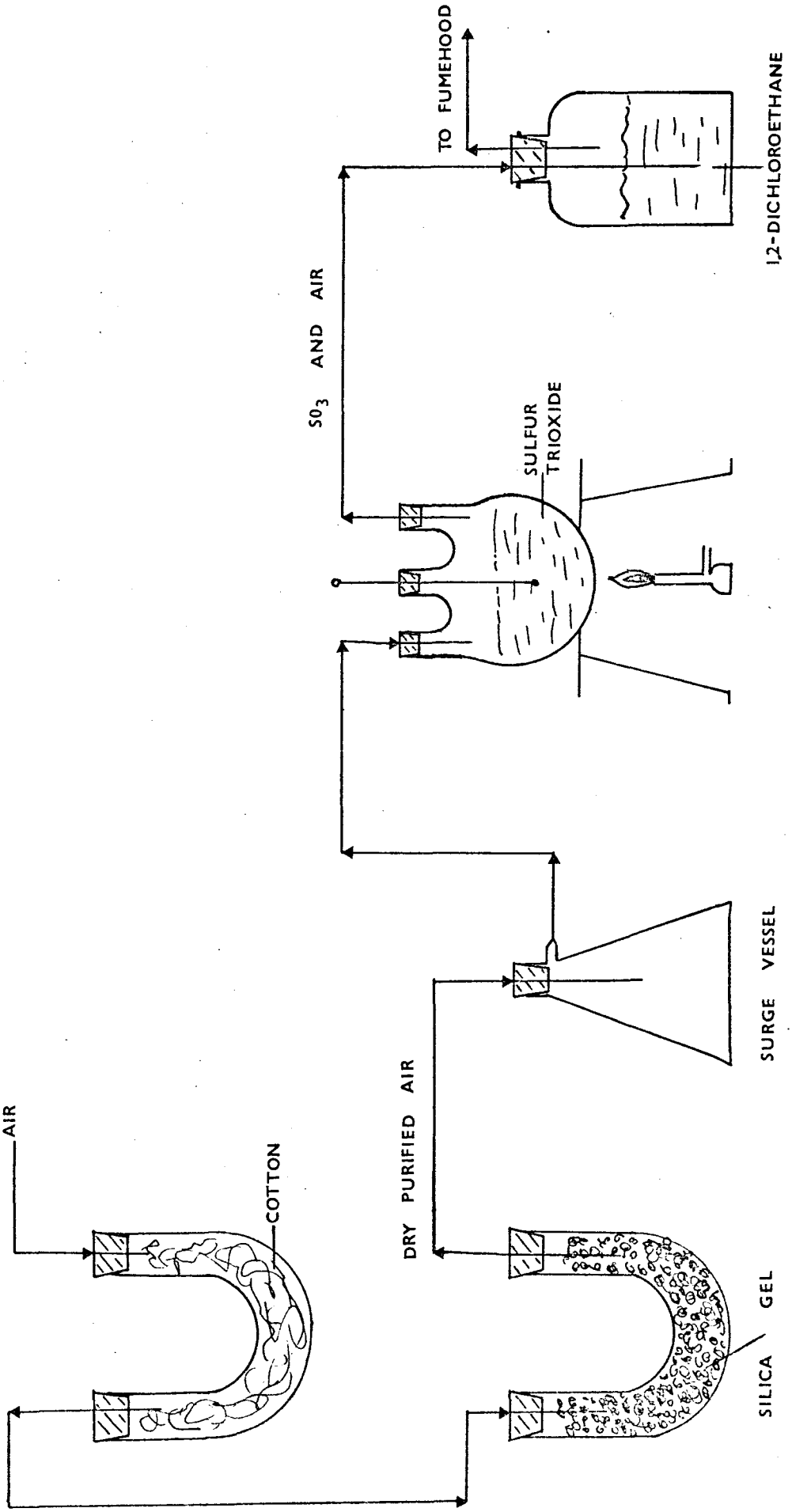


FIG. 3 EXPERIMENTAL APPARATUS - I

trioxide solution and dodecylbenzene solution is placed in their respective feed tanks. Depending on the required concentration of sulfur-trioxide and dodecylbenzene during a particular run 1,2-dichloroethane is added to the feed tanks.

Figure 4 shows the apparatus where the reaction is carried on. The reaction temperature is 29°C.

500c.c. of the sulfur-trioxide solution in 1,2-dichloroethane is allowed to flow straight into the reactor where it is heated to a constant temperature of 29°C. This solution is stirred by a glass stirrer.

Dodecylbenzene solution in 1,2-dichloroethane from the feed tank is allowed to flow to another holding vessel where it is heated to 29°C. This solution is stirred by a magnetic stirrer.

Constant temperature is maintained by connecting a thermoregulator and a heater to a CRC Monitor Relay. The heater is connected through a transformer for temperature control. The relay is connected to the main line. The reaction temperature 29°C is set on the thermoregulator by rotating the collar located at the top of the instrument. When the liquid temperature is 29°C the heater goes off. The exact temperature is obtained by a "built-in" thermometer in the thermoregulator. The relay gives temperature control within ± 0.01°C.

Dodecylbenzene solution is allowed to flow from the holding tank to a 500c.c. flask equipped with a thermometer.

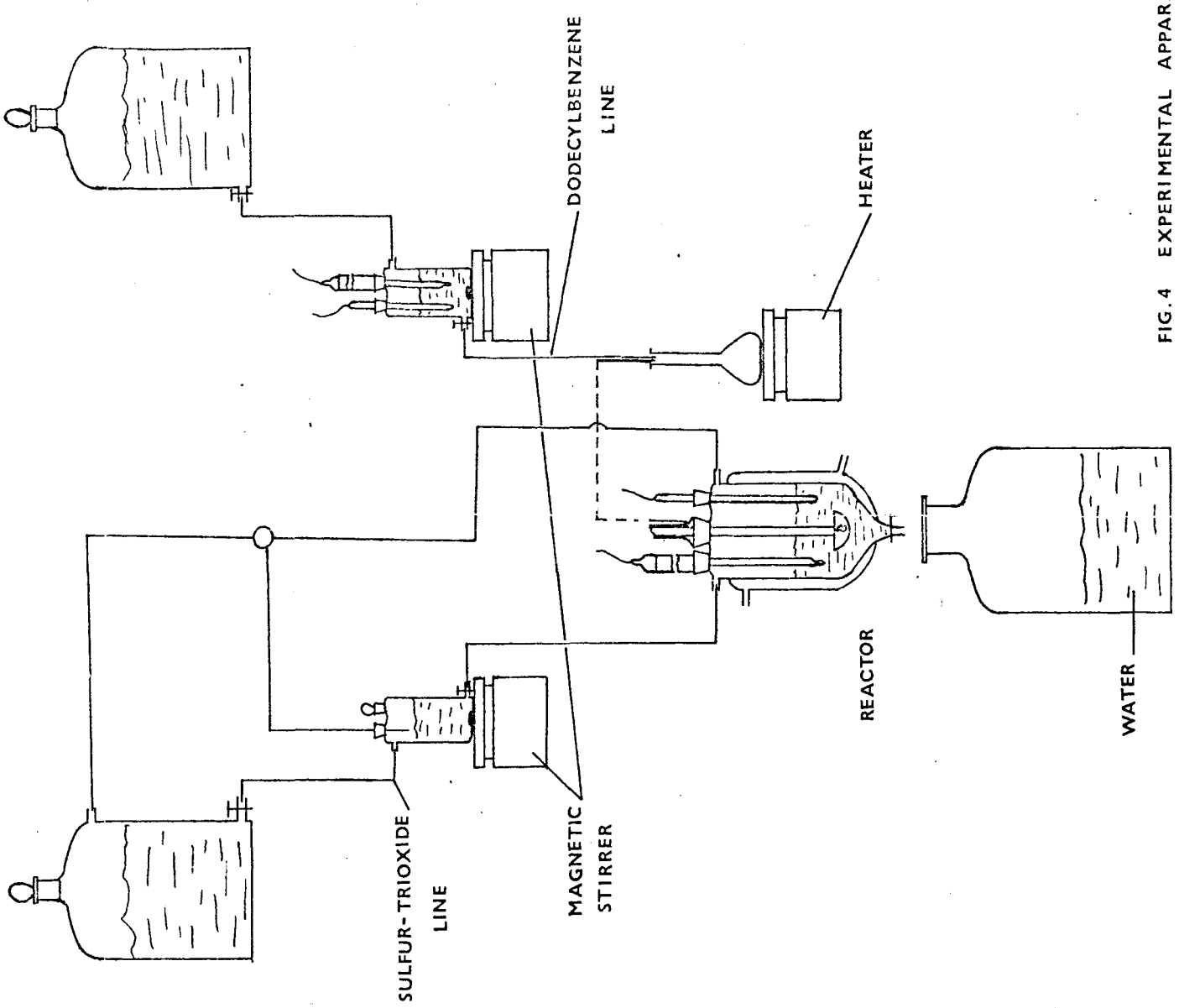


FIG. 4 EXPERIMENTAL APPARATUS - 2

The flask is kept on a heater, the temperature noted and the solution heated if necessary. The dodecylbenzene solution is poured into the reactor and the reaction is carried out for a certain length of time. This time is recorded. The reaction mass is stirred during this time. To stop the reaction the whole reaction mass is dumped into 2000c.c. of water. This is done by opening a stopcock at the bottom of the reactor. Same procedure is followed for different reaction times.

Dodecylbenzene concentration is kept constant. For a particular sulfur-trioxide concentration the above procedure is carried out to obtain the change of concentration with time. Sulfur-trioxide concentration is changed to obtain a set of similar data.

Then sulfur-trioxide concentration is kept constant and dodecylbenzene concentration is varied. Again a set of data is obtained for change of concentration with time.

The extent of sulfonation of dodecylbenzene by sulfur-trioxide is measured by the acidity of 1,2-dichloroethane emerging from the reactor. The residual sulfur-trioxide and sulfonic acid is extracted when the reaction mass is dumped into water. The water layer is titrated with standard sodium hydroxide and the acidity measured. The sulfur-trioxide present initially is found by similarly extracting with water and measuring the acidity. If the reaction is complete the acidity will be half.

The amount of sulfur-trioxide reacted is obtained and

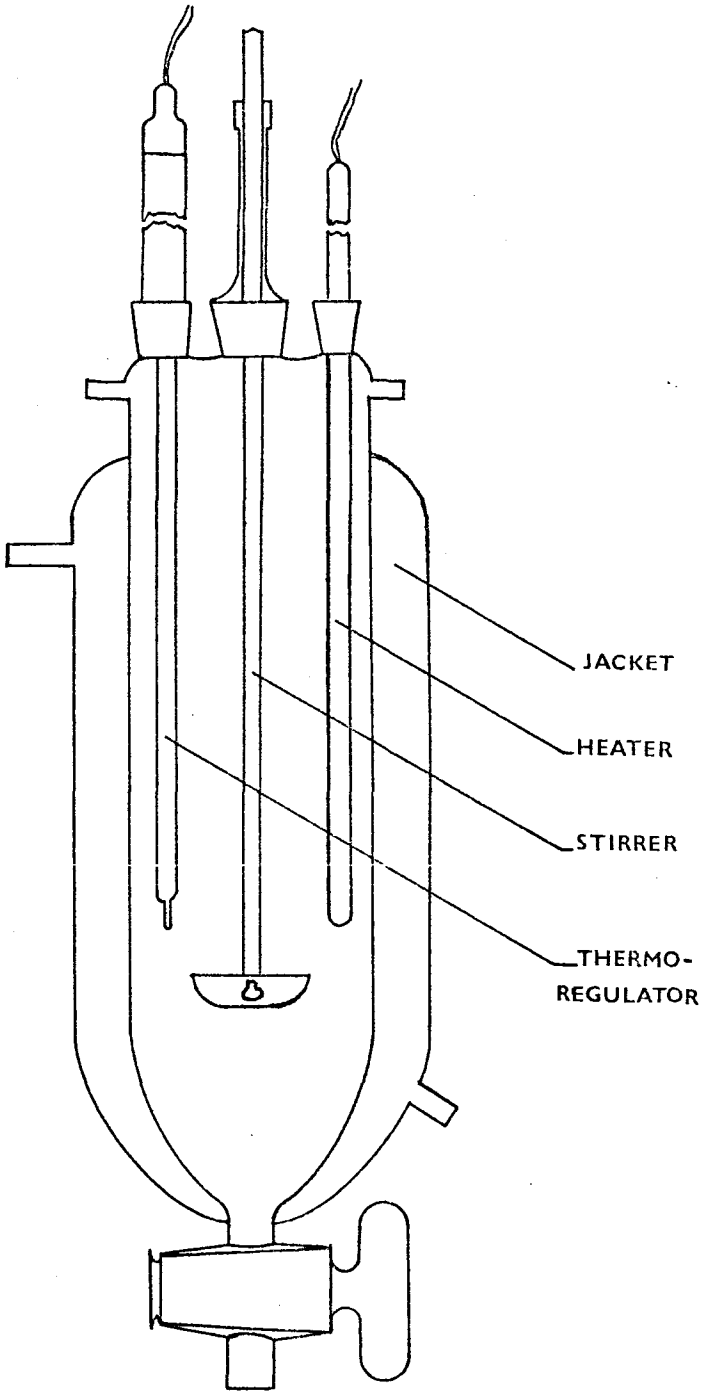
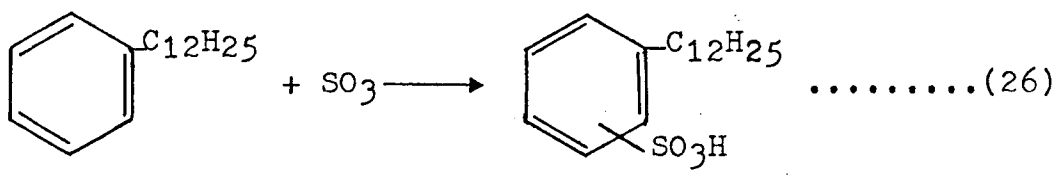


FIG. 5 REACTOR

therefore the concentration of sulfur-trioxide remaining can be calculated. Dodecylbenzene reacted and sulfonic acid formed can be calculated by making use of the following equation.



.....(26)

B. SOLVENT

As seen above, the solvent is required to have certain properties as it has to be satisfactorily inert. The properties required are:

(1) Solvent property for sulfur-trioxide, aromatic hydrocarbon and sulfonic acid

(2) Inertness to sulfur-trioxide, aromatic hydrocarbon and sulfonic acid

(3) Inertness to water

and, (4) Immiscibility in water

Solvents include liquid sulfur-dioxide, n-hexane, tetrachloroethylene, 1,2-dichloroethane, Freon-11, carbon tetrachloride (at $0^{\circ}C$), nitrobenzene, chlorobenzene etc.

Two solvents are found to have almost all the above properties- 1,2-dichloroethane and tetrachloroethylene. But, solution of sulfur-trioxide in tetrachloroethylene is not very stable. The acidity of the solution increases by 37% in twelve days. The possible reaction might be: (7)

$$2SO_3 + C_2Cl_4 \longrightarrow 2SO_2 + 2COCl_2 \quad \text{.....(27)}$$

$$COCl_2 + H_2O \longrightarrow CO_2 + 2HCl \quad \ldots\ldots\ldots\ldots\ldots\ldots (28)$$

Similarly, it has been found that change in acidity of sulfur-trioxide solution in 1,2-dichloroethane is negligible in eight days(7). Therefore, 1,2-dichloroethane is more suitable and is used as a solvent.

C. MATERIALS OF CONSTRUCTION

Feed tanks, reactor and all other equipment is made of glass. The stirrer in the reactor is made of glass with teflon blades. The magnetic stirrer is teflon coated. The tubings for sulfur-trioxide line are teflon and for dodecylbenzene line are of polyethylene. It is necessary to use these materials as dodecylbenzene and sulfur-trioxide are both corrosive compounds. They tend to destroy the tubings completely if constructed of any other material except glass and 316 stainless steel.

D. ANALYTICAL METHOD

To show, that on reaction, dodecylbenzene sulfonic acid is obtained certain analytical methods are used. Dodecylbenzene sulfonic acid and sulfuric acid is present in the water layer after extraction. 10c.c. of the water layer is titrated with standard sodium hydroxide solution. This gives the total hydrogen ion, that is, the amount of acid present.

(a) Let, X be the number of gms. of sulfuric acid
and, Y be the number of gms. of sulfonic acid

Equivalent weight of sulfuric acid = 49

Equivalent weight of sulfonic acid = 326

Therefore,

Number of equivalent of sulfuric acid = X/49

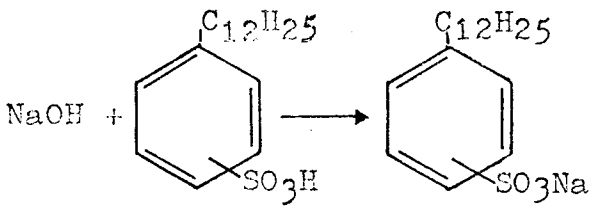
Number of equivalent of sulfonic acid = Y/326

Then, X/49 + Y/326 = number of equivalent of sodium hydroxide required for neutralization .....(29)

(b) 100c.c. of the water is titrated with sodium hydroxide till the acid is neutralized. The compounds obtained on neutralization are sodium sulfate, sodium salt of the sulfonic acid and water. The water is evaporated and the weight of the residue is obtained.

From the reactions given below:

$$2NaOH + H_2SO_4 \longrightarrow Na_2SO_4 + 2H_2O \quad .....(30)$$



X gms. of sulfuric acid gives 142X/98 gms. sodium sulfate

Y gms. of sulfonic acid gives 348Y/326 gms. sodium salt of the sulfonic acid. Therefore,

142X/98 + 348Y/326 = weight of the residue after neutralization .....(32)

From equations (29) and (32), gms. of sulfuric acid and sulfonic acid can be calculated. Knowing the amount of sulfuric acid just enough barium hydroxide is added so as to neutralize sulfuric acid only. Barium sulfate is filtered off. Filtrate now contains dodecylbenzene sulfonic acid and water. Water is evaporated off. Infrared and Nuclear Magnetic

Resonance spectrum is run on the residue which is dodecylbenzene sulfonic acid. Before doing this an Infrared spectrum is obtained on commercial dodecylbenzene sample from Fisher Scientific Company and a Nuclear Magnetic Resonance spectrum is obtained on the dodecylbenzene sulfonic acid sample from Continental Oil Company.

V. RESULTS

Results are summarized in Appendix.

A number of trial runs were made initially to get the apparatus to the exact working conditions of temperature, volume, concentration etc. The final runs were then started.

The first six runs were taken at constant dodecylbenzene concentration. Plots were made for each run by taking time on the abscissa and log(concentration) on the ordinate. The plots are extrapolated to time T=0(Figs.6,7,8). Tangents are drawn to these plots at T=0. The slope of the tangent is $-d(\log C_i)/dT = -\frac{1}{C_i} \cdot (dC_i/dT)$ .....(33)

The initial reaction rate $-dC_i/dT$ was calculate from the above equation (33). The errors in measuring the rates were thereby minimized. The results are given in Table 3.

From these results a plot of log(initial rate) versus log(initial concentration) is drawn. This plot is linear as shown in Fig.9 The best linear equation fitting these data is found by the method of least squares to be:

$$-dC_i/dT = 2.05\ C_{Si}^{1.785} \quad \text{.....(34)}$$

The next six runs were made at constant sulfur-trioxide concentration. The dodecylbenzene concentration is varied and similar plots of time versus log(dodecylbenzene concentration) are obtained. The results are shown in Figs.10,11. Initial reaction rates are found as before. The results are given in Table 4.

TABLE 3

Results for Constant Dodecylbenzene Concentration

C_{Hi} = 0.2217 gm.moles/lit.

Run no.	Initial SO_3 conc. gm.moles/litre	Initial reaction rate gm.moles per litre per sec
1	0.0370	0.00637
2	0.0653	0.01682
3	0.0600	0.01320
4	0.0470	0.00894
5	0.0610	0.01400
6	0.0432	0.00648

TABLE 4

Results for Constant Sulfur-trioxide Concentration

C_{Si} = 0.04 gm.moles/litre

Run no.	Initial DDB conc. gm.moles/litre	Initial reaction rate gm.moles per litre per sec
7	0.1200	0.00598
8	0.1000	0.00540
9	0.0800	0.00464
10	0.0900	0.00475
11	0.1150	0.00557
12	0.0850	0.00498

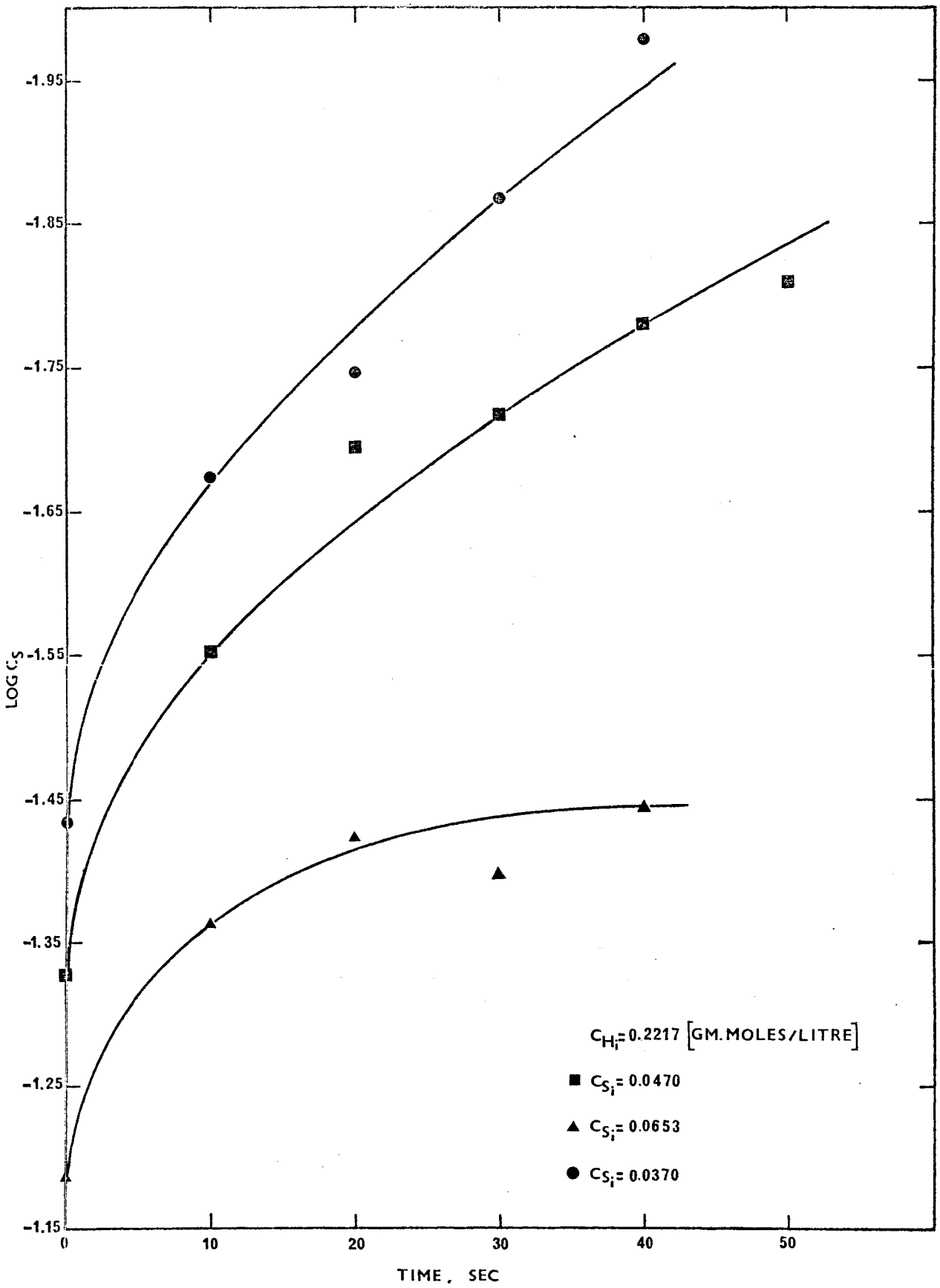


FIG. 6 VARIATION OF SULFUR-TRIOXIDE CONCENTRATION WITH TIME

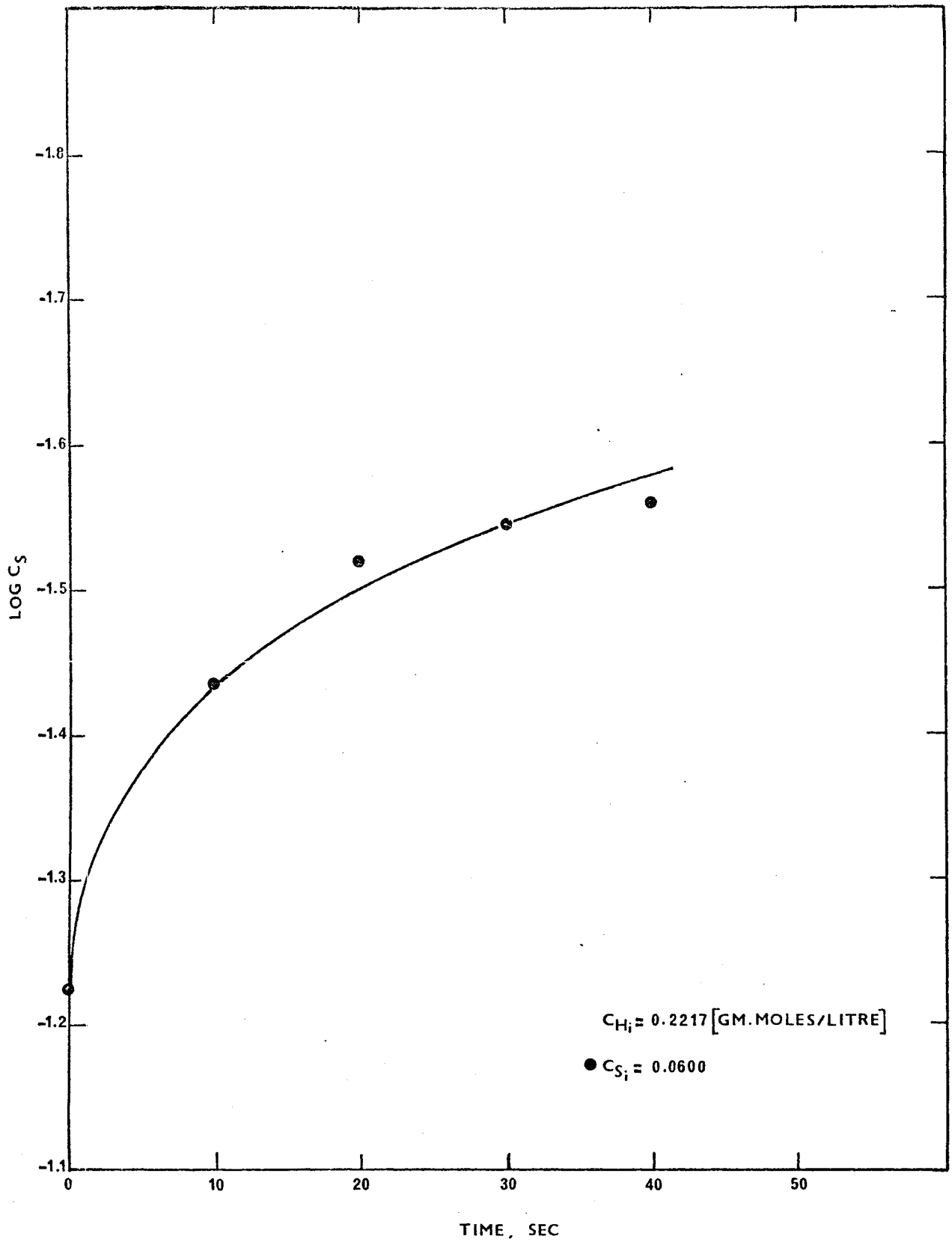


FIG. 7 VARIATION OF SULFUR-TRIOXIDE CONCENTRATION WITH TIME

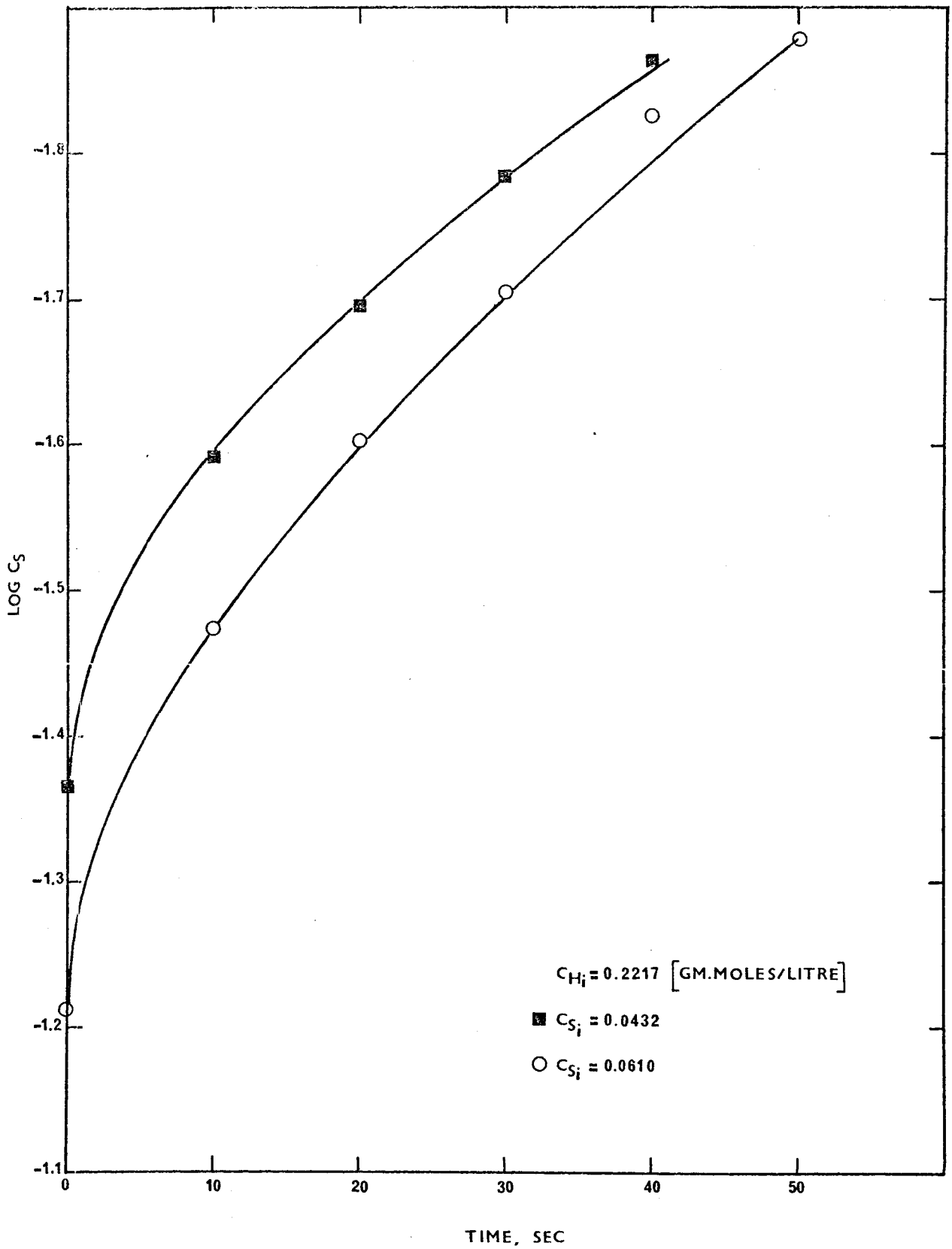


FIG. 8 VARIATION OF SULFUR-TRIOXIDE CONCENTRATION WITH TIME

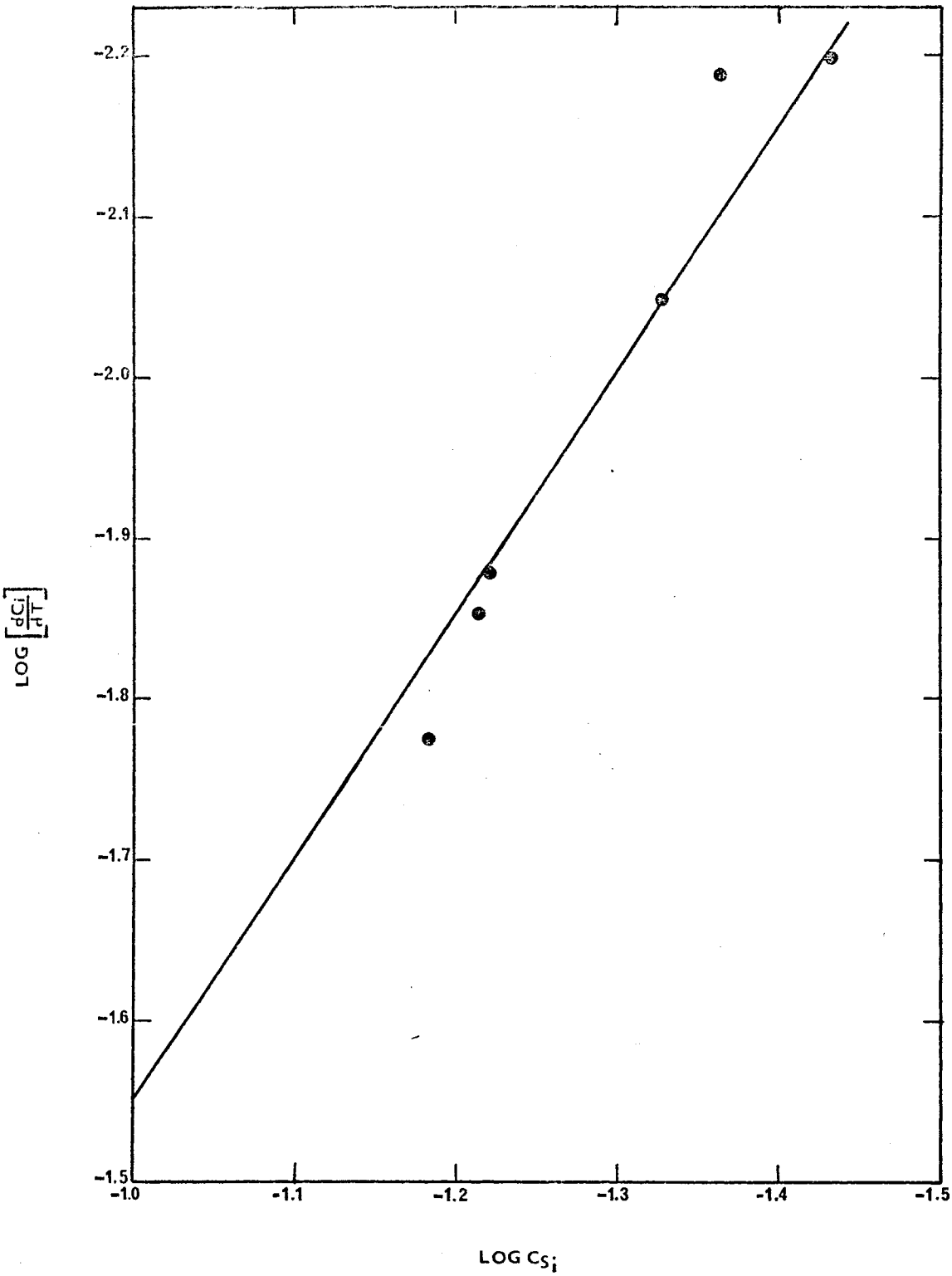


FIG. 9 VARIATION OF INITIAL REACTION RATE WITH SULFUR-TRIOXIDE CONCENTRATION

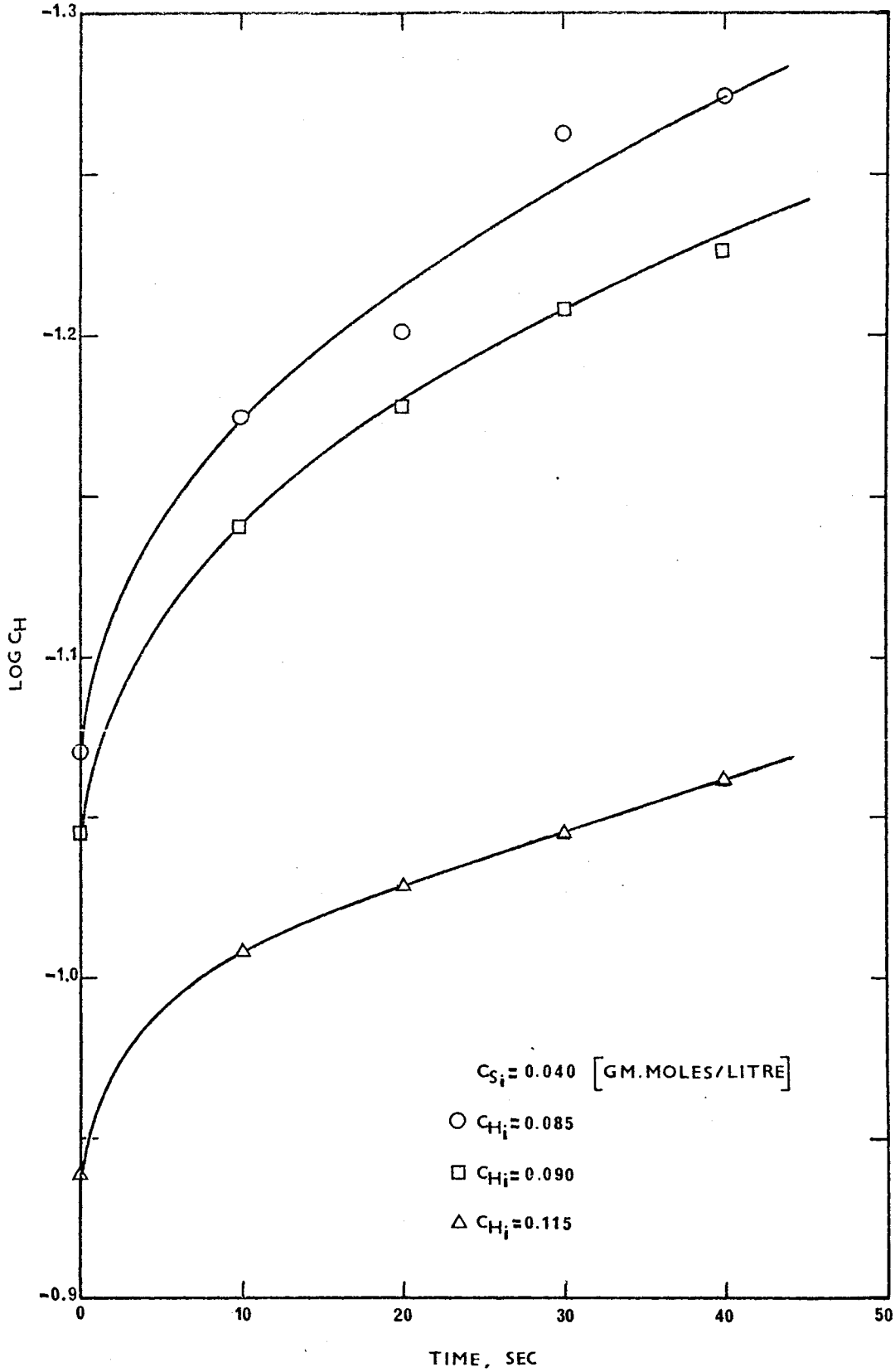


FIG. 10 VARIATION OF DODECYL BENZENE CONCENTRATION WITH TIME

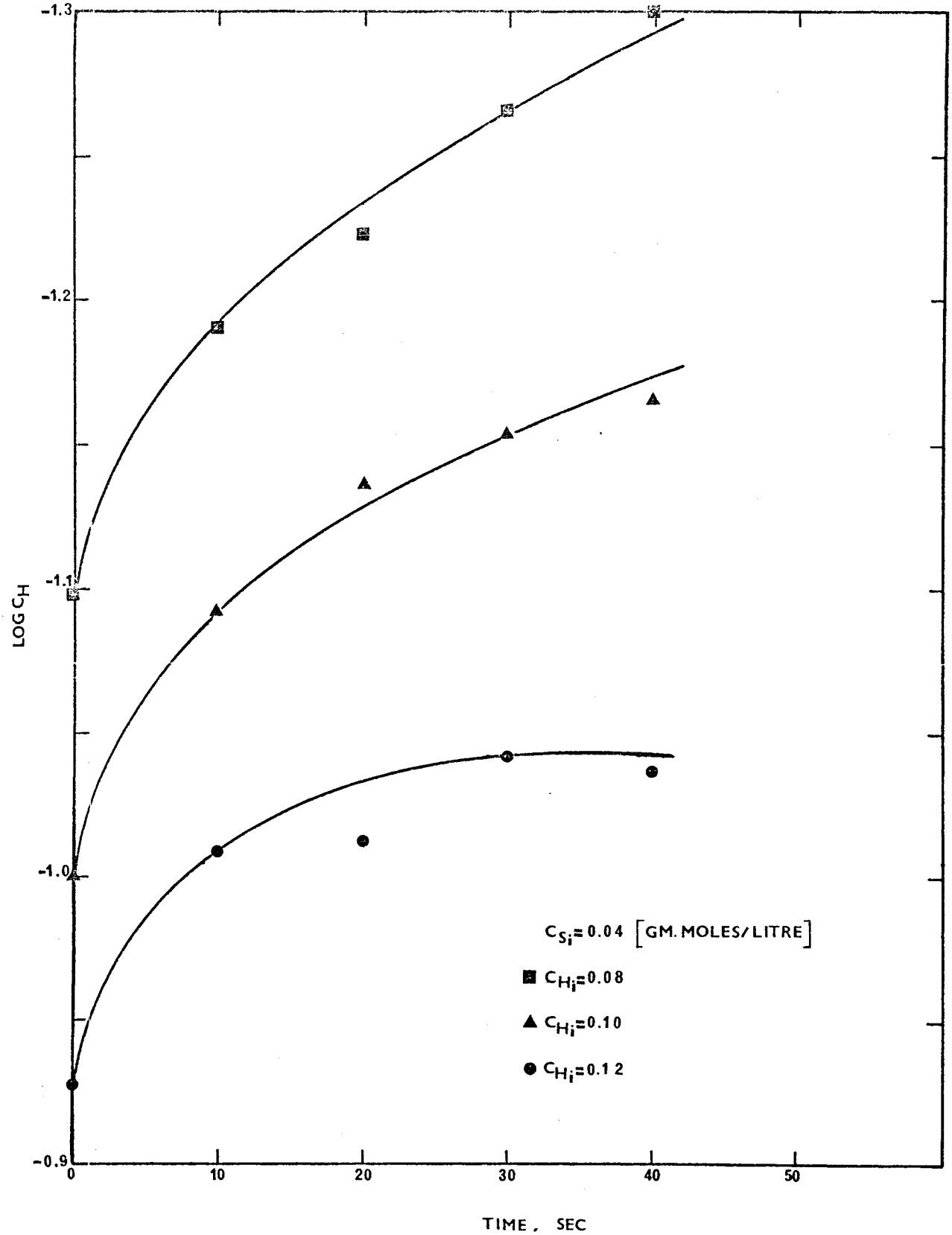


FIG.11 VARIATION OF DODECYL BENZENE CONCENTRATION WITH TIME

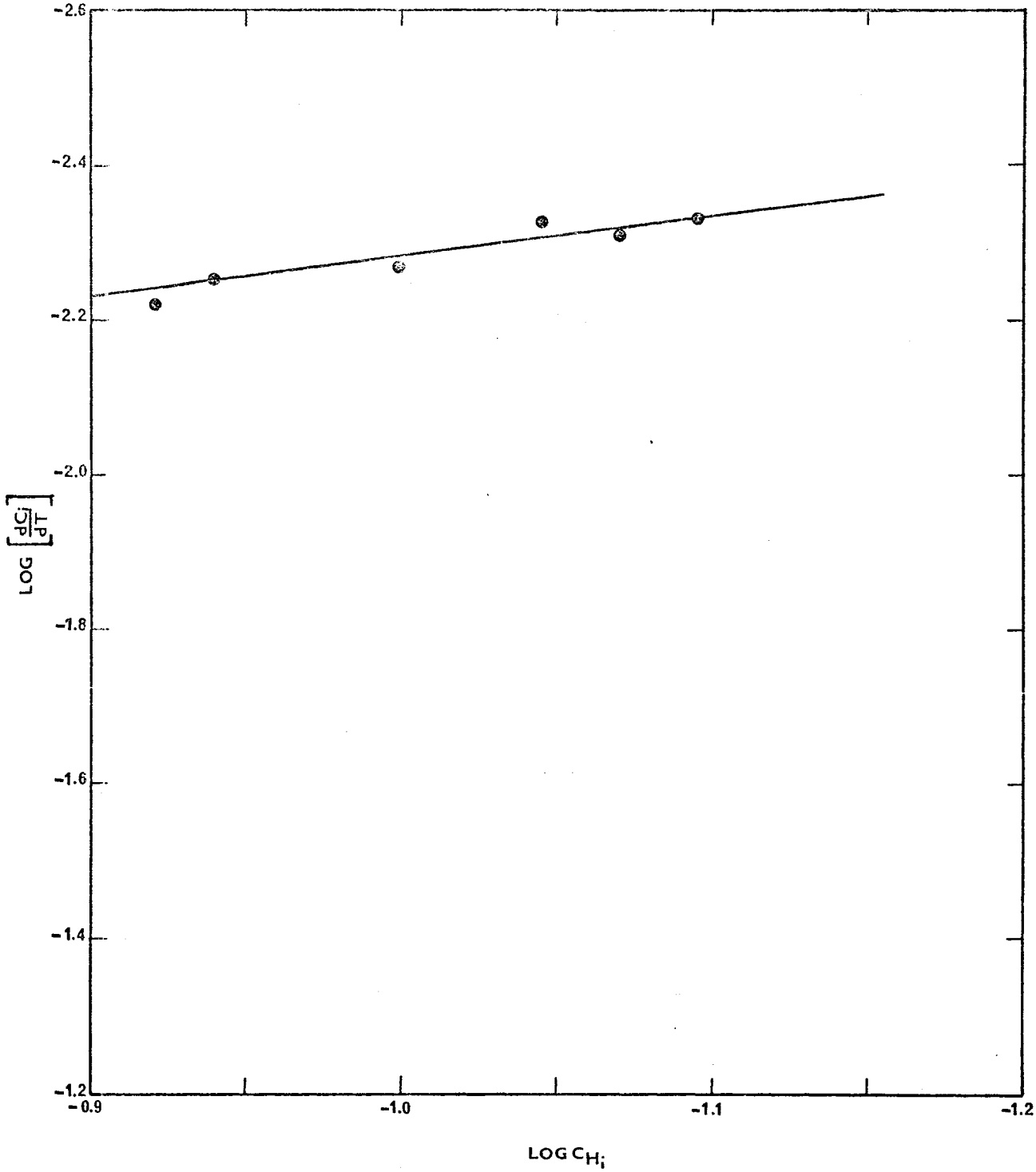


FIG. 12 VARIATION OF INITIAL REACTION RATE WITH DODECYL BENZENE CONCENTRATION

From these results a plot of log(initial rate) versus log(initial concentration) is drawn. This plot is linear as shown in Fig.12. The best linear equation fitting these data is found by the method of least squares to be:

$$-dC_i/dT = 0.0185\ C_{Hi}^{0.563} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(35)$$

From equations (24) and (34),

$$2.05 = k(C_{Hi})^{\alpha} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(36)$$

$$= k(0.2217)^{0.563} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(37)$$

Therefore, $k = 4.87$

$$\text{Then, } -dC_i/dT = 4.87\ C_{Hi}^{0.563}\ C_{Si}^{1.785} \quad \ldots\ldots\ldots\ldots\ldots(38)$$

Also, from equations (22) and (35),

$$0.0185 = k(C_{Si})^{\beta} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(39)$$

$$= k(0.04)^{1.785} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(40)$$

Therefore, $k = 5.78$

$$\text{Then, } -dC_i/dT = 5.78\ C_{Hi}^{0.563}\ C_{Si}^{1.785} \quad \ldots\ldots\ldots\ldots\ldots(41)$$

Taking an average:

$$-dC_i/dT = 5.325\ C_{Hi}^{0.563}\ C_{Si}^{1.785} \quad \ldots\ldots\ldots\ldots\ldots(42)$$

From the final equation (42) log(initial rate) is calculated and compared with that obtained experimentally (Table 13 in Appendix). For the data, multiple correlation coefficient is:

$$r = 0.9545$$

Similarly, rates are compared to obtain :(Table 14 in Appendix)

$$r = 0.9674$$

The value of multiple correlation coefficient obtained in

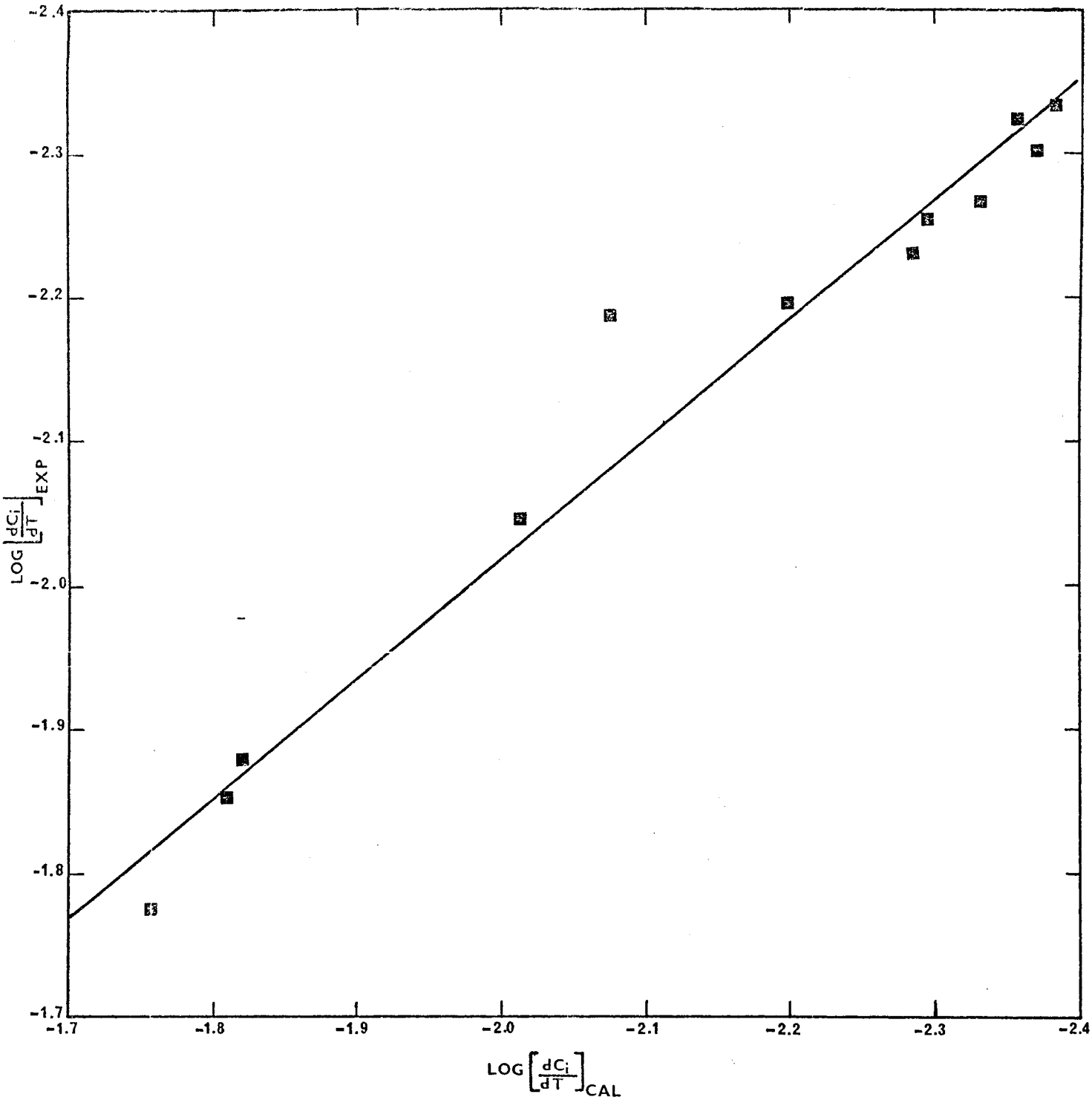


FIG. 13 COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED INITIAL REACTION RATES

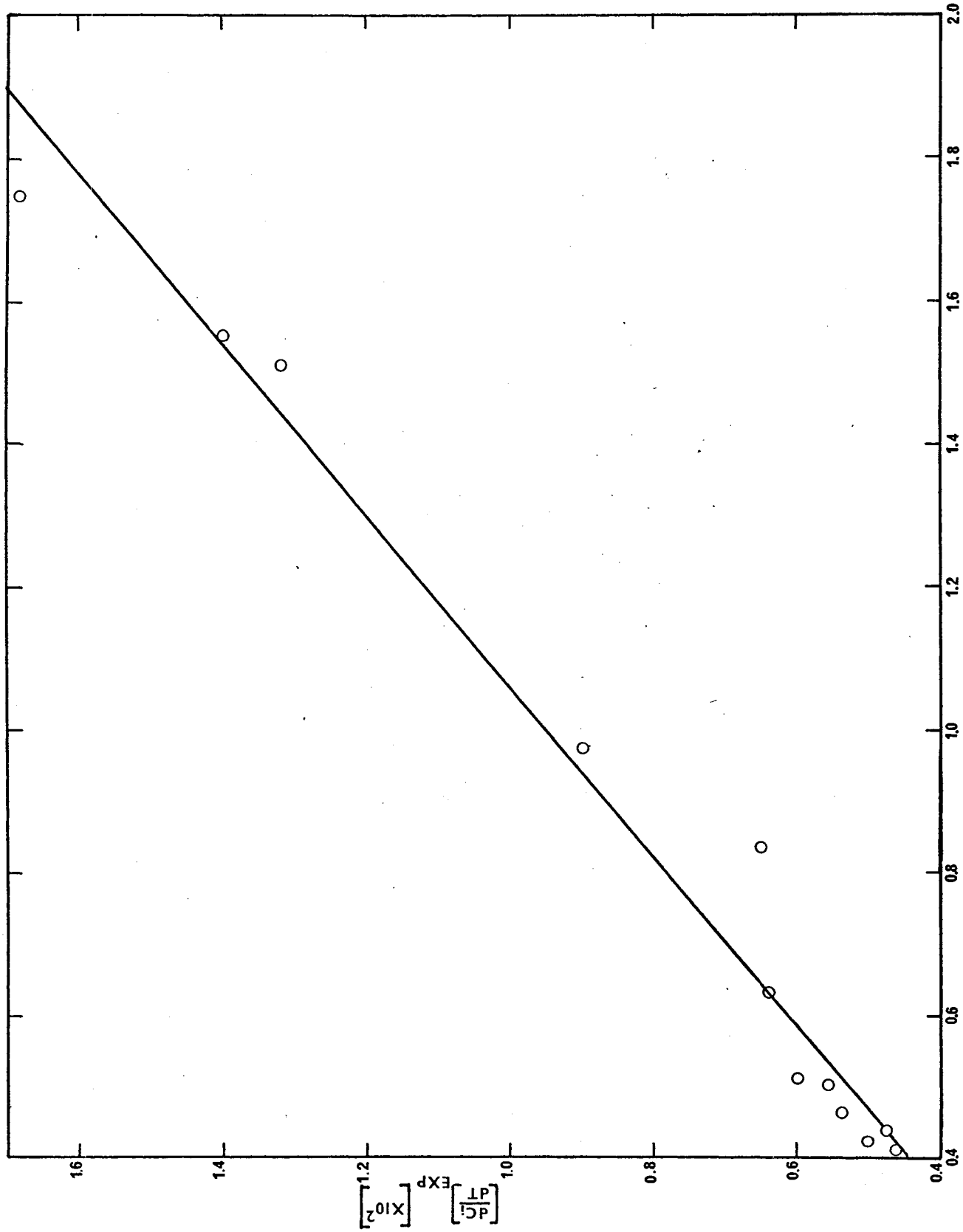


FIG.14 COMPARISON BETWEEN EXPERIMENTAL AND CALCULATED INITIAL REACTION RATES

both cases is greater than the value obtained from the statistical tables at the 95% level. This shows that the correlation is good.

Analysis:

Nuclear Magnetic Resonance and Infrared spectra are run on the sample obtained after separating sulfuric acid. The sample is expected to be sulfonic acid of dodecylbenzene.

Infrared:

The spectrum in Fig. 15 is of commercial dodecylbenzene. The spectrum in Fig. 16 is the unknown which is expected to be dodecylbenzene sulfonic acid. The unknown spectrum will be different from the dodecylbenzene spectrum because of the additional $-SO_3H$ group. There will be some extra peaks due to this group. As seen, these peaks are at the wavenumbers 1000 cm^{-1}, 660 cm^{-1}, 1125 cm^{-1} and 1160 cm^{-1}. The peaks at 1000 cm^{-1} and 660 cm^{-1} are due to the sulfonic acid group. The broad peaks at 1125 cm^{-1} and 1160 cm^{-1} are due to out of plane -CH bending - symmetric and assymetric. Other peaks are the same, which can be explained as follows:

There are distinct sharp peaks at 1600 cm^{-1} and 1500 cm^{-1} showing presence of C=C in benzene ring.This establishes the presence of benzene ring in the compound. Also, showing the presence of benzene ring is the peak at 3080 cm^{-1} due to -CH stretching in -C=C-H. Peaks at 3000 cm^{-1}, 2960 cm^{-1}, 2925 cm^{-1} and 2865 cm^{-1} are due to symmetrical and asymetrical -CH stretching in methyl($-CH_3$) and methylene($-CH_2-$) groups. Peaks at 1450 cm^{-1} and 1420 cm^{-1} are due to asymmetric

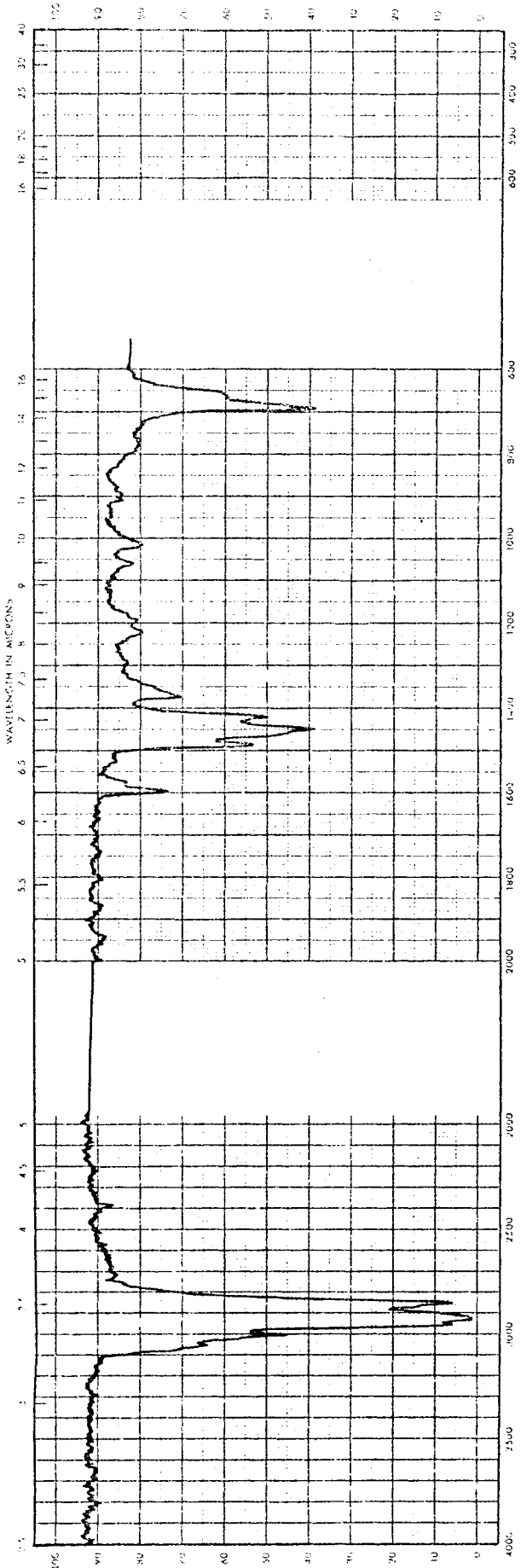


FIG. 15 INFRARED SPECTRUM OF DODECYL BENZENE

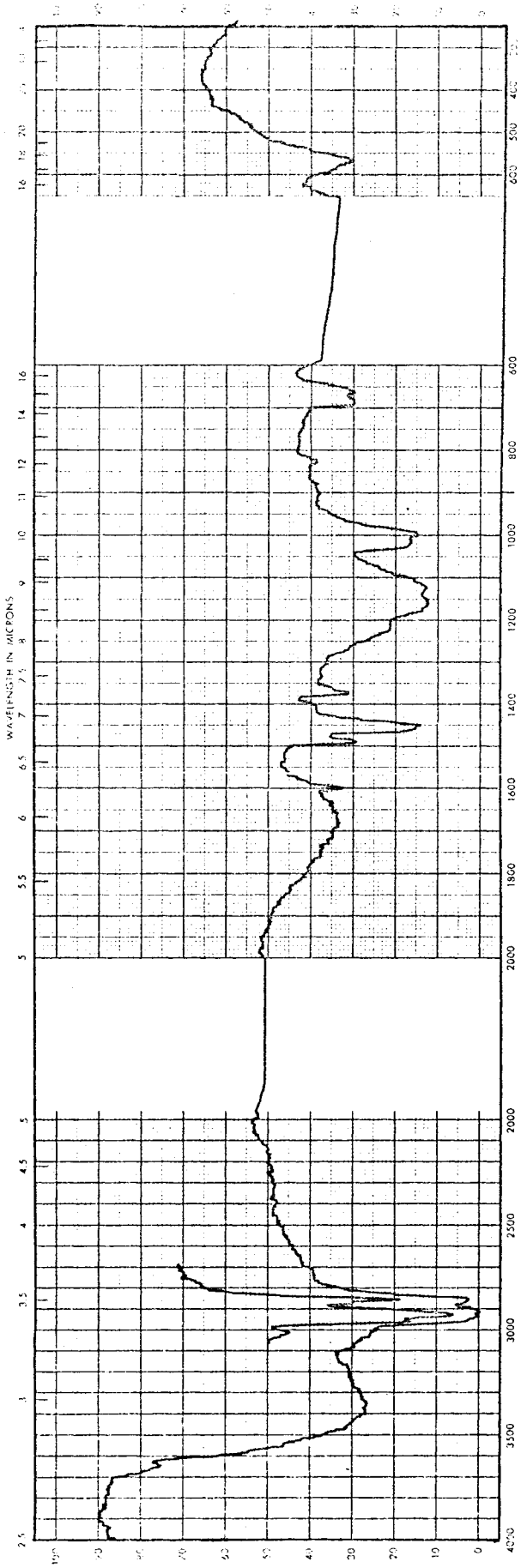
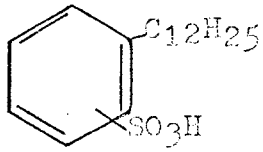


FIG. 16 INFRARED SPECTRUM OF DODECYL BENZENE SULFONIC ACID

methyl bending (and, may be methylene scissoring) and at 1375 cm^{-1} due to symmetrical methyl bending.

Looking at the above description of the two Infrared spectra the compound formed and present in the sample is definitely



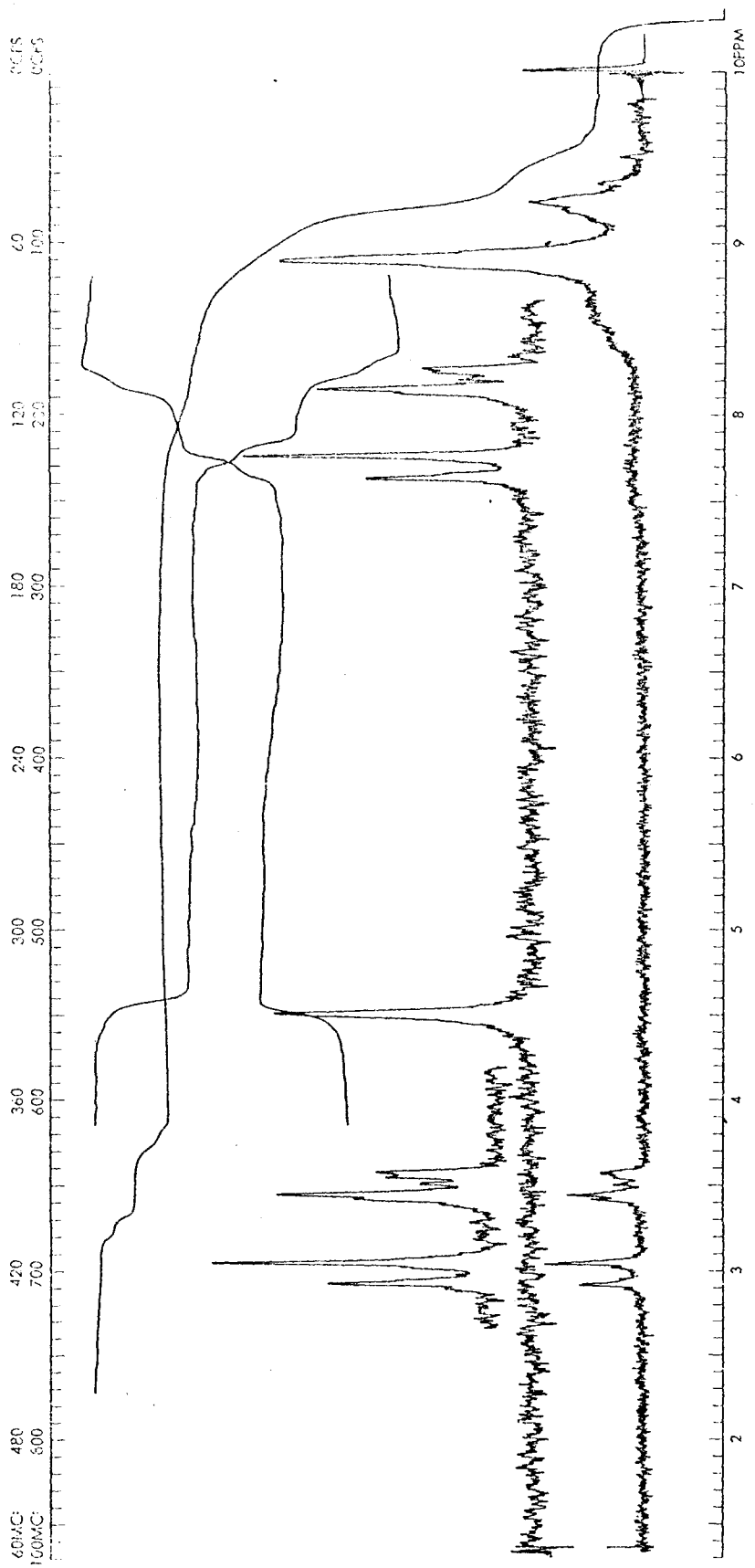
Nuclear Magnetic Resonance:

Fig. 17 shows Nuclear Magnetic Resonance spectrum of standard dodecylbenzene sulfonic acid obtained from Continental Oil Company. On integration, from NMR:

TABLE 5

Chemical shift τ	Intensity
9.25	6
8.85	18
8.50	1
3.45	2
2.95	2
-1.25	1
	Total 30

Number of protons are 30. There are 4 protons at the peaks at $\tau = 3.45$ and $\tau = 2.95$. At these peaks the protons are the benzene ring protons. Therefore, the compound is di-substituted and para-substituted. There is a single proton



CHEMICAL SHIFT

FIG. 17 NUCLEAR MAGNETIC RESONANCE SPECTRUM OF STANDARD DODECYL BENZENE SULFONIC ACID

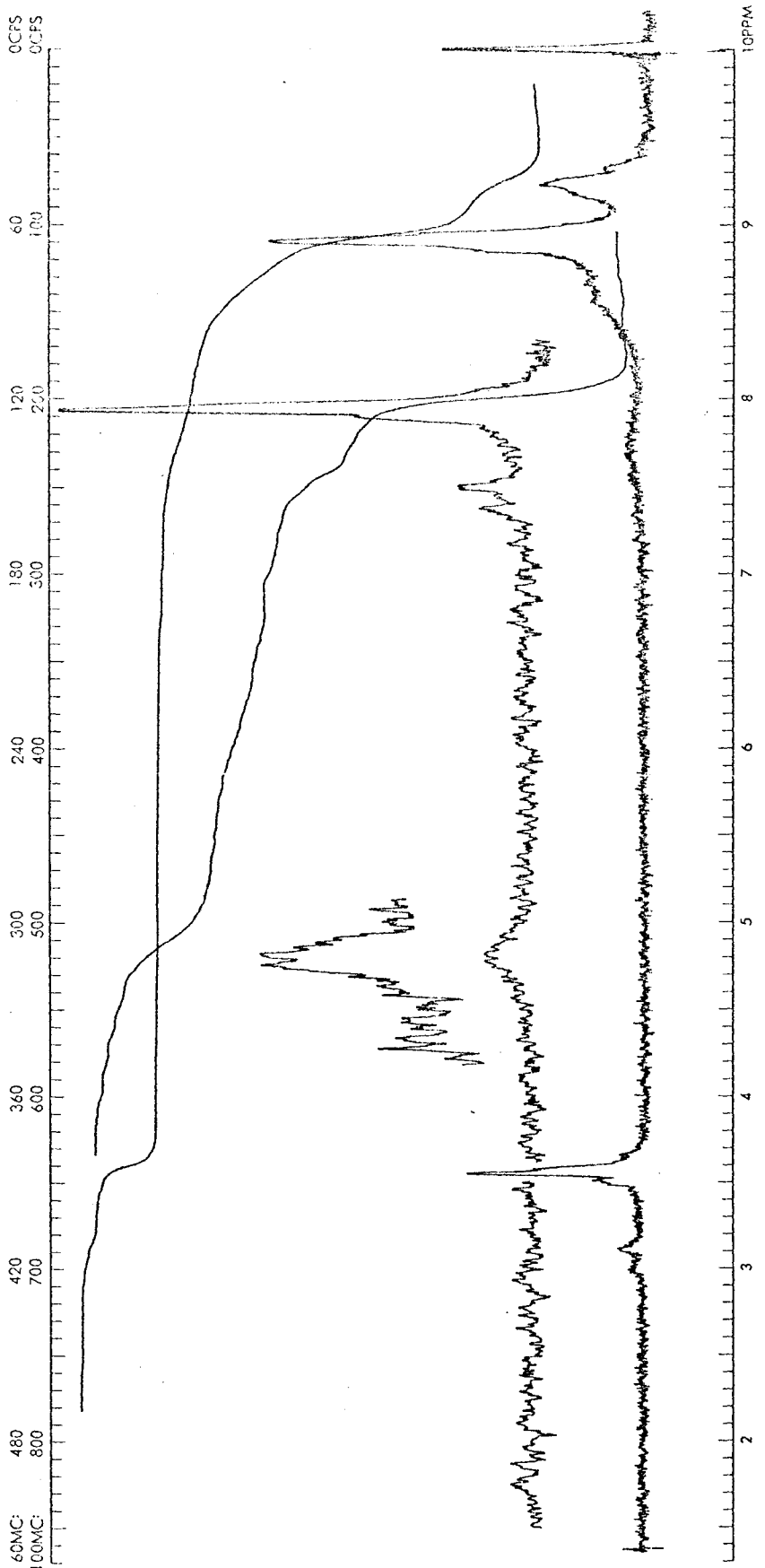


FIG. 18 NUCLEAR MAGNETIC RESONANCE SPECTRUM OF DODECYL BENZENE SULFONIC ACID FROM REACTION PRODUCT

at τ = -1.25 which is definitely an acidic proton in $-SO_3H$ group. This leaves 25 protons which would be due to the other substituent $-C_{12}H_{25}$.

Studying the NMR of the unknown sample (Fig. 18) it is seen that the spectrum is the same as the known sample except there is a single peak at τ = 4.45 for all the 4 protons instead of two separate peaks for two protons each. This is due to the fact that it is not possible to obtain only para-substituted compound on reaction. Normally a mixture of ortho, meta and para-substituted compound is obtained, the percentage of which varies depending on the presence of the directing group. This is the original substituent $-C_{12}H_{25}$, which is, ortho-para directing. The compound is therefore, dodecylbenzene sulfonic acid.

From complete analysis by IR and NMR it is shown that the compound obtained on reaction is definitely dodecyl-benzene sulfonic acid.

VI. RECOMMENDATIONS

The rate equation obtained at 29°C for the reaction between dodecylbenzene and sulfur-trioxide in 1,2-dichloroethane is:

$$-dC_i/dT = 5.325\ C_{H_i}^{0.563}\ C_{S_i}^{1.785} \quad \text{.....(43)}$$

There is a further scope for experimental work with this system. This work can be repeated at other temperature so as to obtain activation energy.

Lower or higher homologues of the hydrocarbon can be used to obtain similar data. It may also be possible to use other solvents instead of 1,2-dichloroethane.

BIBLIOGRAPHY

1. Snell, C.T. and F.D. Snell, Synthetic Detergents Manufacture from Petrochemicals, The Petroleum Engineer, C-7, (December, 1954).

2. Vicary, D.R. and C.N. Hinshelwood, The Kinetics of the Sulfonation of Nitrobenzene by Sulfur-trioxide, Chemical Society of London Journal, p. 1372, (1939).

3. Wadsworth, K.D. and C.N. Hinshelwood, The Kinetics of Aromatic Sulfonation Reactions: The Sulfonation of p-nitrotoluene and of Chlorobenzene by Sulfur-trioxide, Chemical Society of London Journal, p. 469 (1944).

4. Michael, A. and N.Weiner, Sulfonation Process, Journal of American Chemical Society, 58, p. 294, (1936.

5. Dresel, E. and C.N. Hinshelwood, The Kinetics of the Sulfonation of some Aromatic Compounds by Sulfur-trioxide, Chemical Society of London Journal, p. 649 (1944.

6. Leierson, Dost and LeBaron, Liquid Sulfur-dioxide in Sulfonation of Benzene, Industrial and Engineering Chemistry, 40, p. 508, (1948).

7. Ratcliffe, G.A., Kinetics of Sulfonation Reaction, Ph.D. Dissertation, Cornell University, Ithaca, New York, (1954).

8. Royle, A.T., Stabilized Liquid Sulfur-trioxide, Industrial Chemist, p. 421, (October, 1956).

9. Guyot, Nauveau Procede de Sulfonation des Carbures Benzeniques, Chimie et Industrie, 2, p. 879, (1919).

10. Courtot, C., The value of Sulfonation, Compt. rend., 182, p. 855, (1926).

11. Spryskov, A.A., Sulfonation Reaction, Journal of General Chemistry of U.S.S.R., 8, p. 1857 (1938).

12. Gilbert, E.E., Sulfonation and related Reactions, Interscience Publishers, New York, (1965).

13. Bueggeberg, W.H.C., T.W. Sauls and S.L. Norwood, On the Mechanism of Sulfonation of the Aromatic Nucleus and Sulfone Formation, Journal of Organic Chemistry, 20, p. 455, (April, 1955).

14. Arkin, H. and R.R. Colton, Statistical Methods, Barnes and Noble, Inc., New York, (1939).

15. Encyclopedia of Chemical Technology, 5, p. 149, Interscience Publishers, New York.

16. Encyclopedia of Chemical Technology, 13, pp. 317, 352, 501, The Interscience Encyclopedia, Inc., New York.

17. Groggins, P.H., Unit Processes in Organic Synthesis, McGraw-Hill Book Co., New York, (1958).

18. Schwartz, A.M. and J.W. Perry, Surface Active Agents, Interscience Publishers, New York, (1949).

19. Perry, R.H., Chemical Engineers' Handbook, 4th ed., McGraw-Hill Book Co., New York.

20. Gilbert, E.E., B. Veldhuis, E.J. Carlson and S.L. Giolit Sulfonation and Sulfation, Industrial and Engineering Chemistry, Series of papers, (1948-1961).

21. Gilbert, E.E. and B. Veldhuis, Sulfonation with Sulfur-trioxide, Industrial and Engineering Chemistry, Series papers, (1953-1958).

APPENDIX

TABLE 6

Summary of Experimental Data

C_{Hi} = 0.2217 gm. moles/litre

Run no.	Time sec	Titre cm^3	Sulfur-trioxide conc.-initial gm. moles/litre	Sulfur-trioxide reacted %
1 A	0	1.250	0.03700	0.00
B	10	0.984		42.50
C	20	0.930		51.40
D	30	0.855		63.50
E	40	0.805		71.60
2 A	0	9.900	0.06530	0.00
B	10	8.170		35.00
C	20	7.820		42.00
D	30	7.970		38.70
E	40	7.700		44.50
3 A	0	8.800	0.06000	0.00
B	10	7.100		38.60
C	20	6.600		50.00
D	30	6.420		54.15
E	40	6.490		52.40
4 A	0	5.700	0.04700	0.00
B	10	4.530		41.00
C	20	4.200		52.63
D	30	4.020		59.20
E	40	3.850		64.91
F	50	3.800		66.66
5 A	0	7.400	0.06100	0.00
B	10	5.820		45.30
C	20	5.220		59.00
D	30	4.900		67.60
E	40	4.600		75.60
F	50	4.500		78.40
6 A	0	6.550	0.04320	0.00
B	10	5.225		40.50
C	20	4.800		53.42
D	30	4.900		61.80
E	40	4.600		67.60
F	50	4.230		70.80

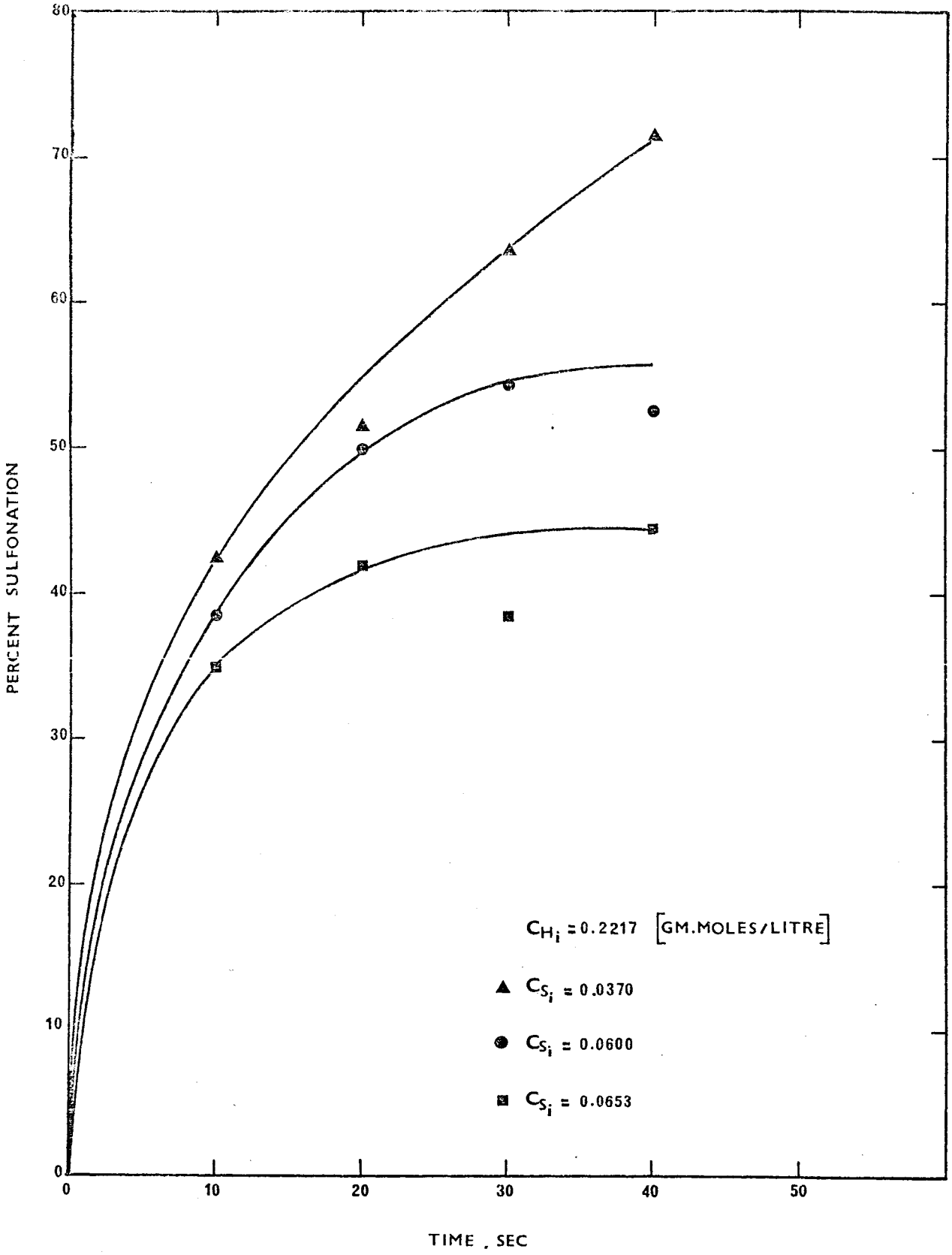


FIG. 19 EXTENT OF SULFONATION

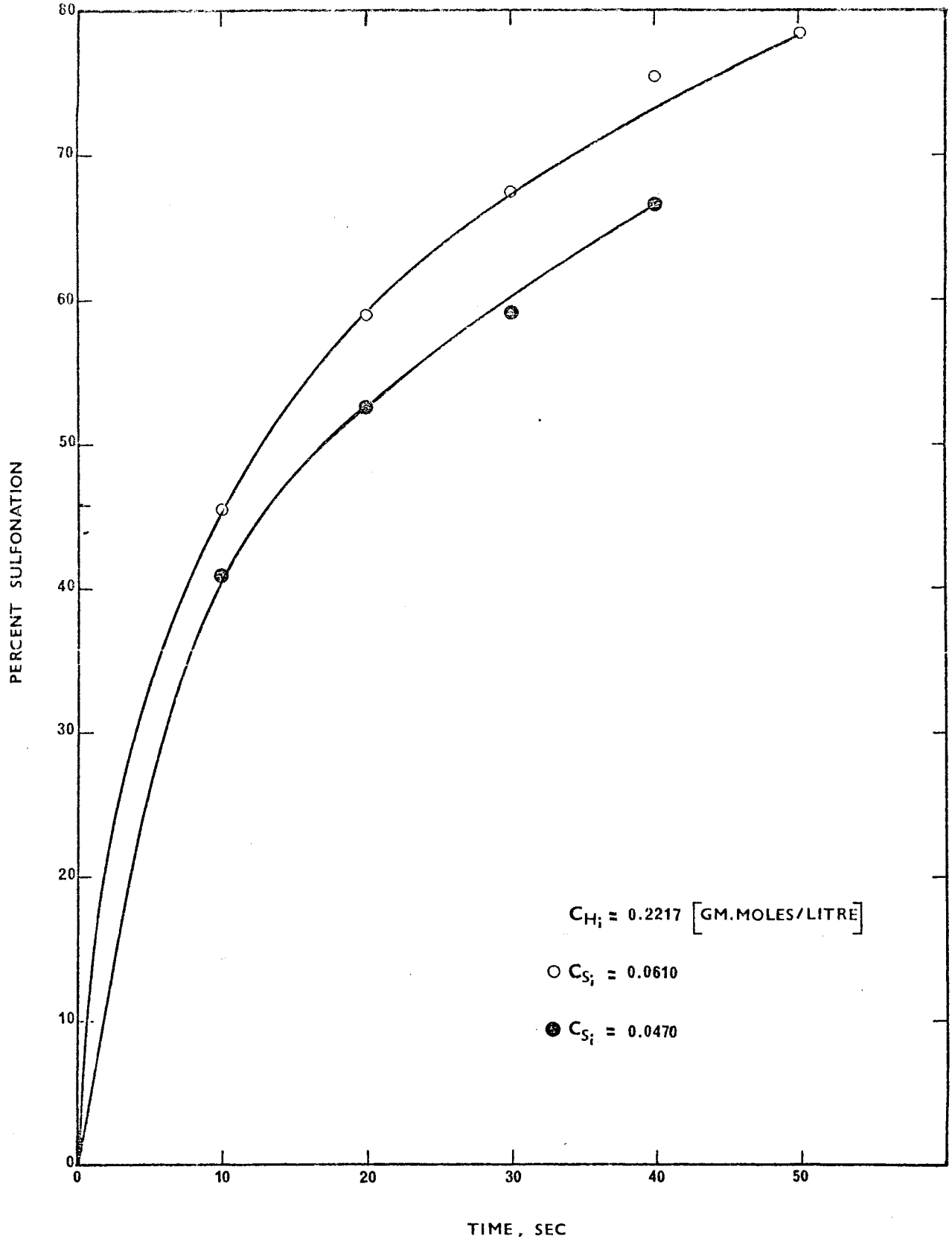


FIG. 20 EXTENT OF SULFONATION

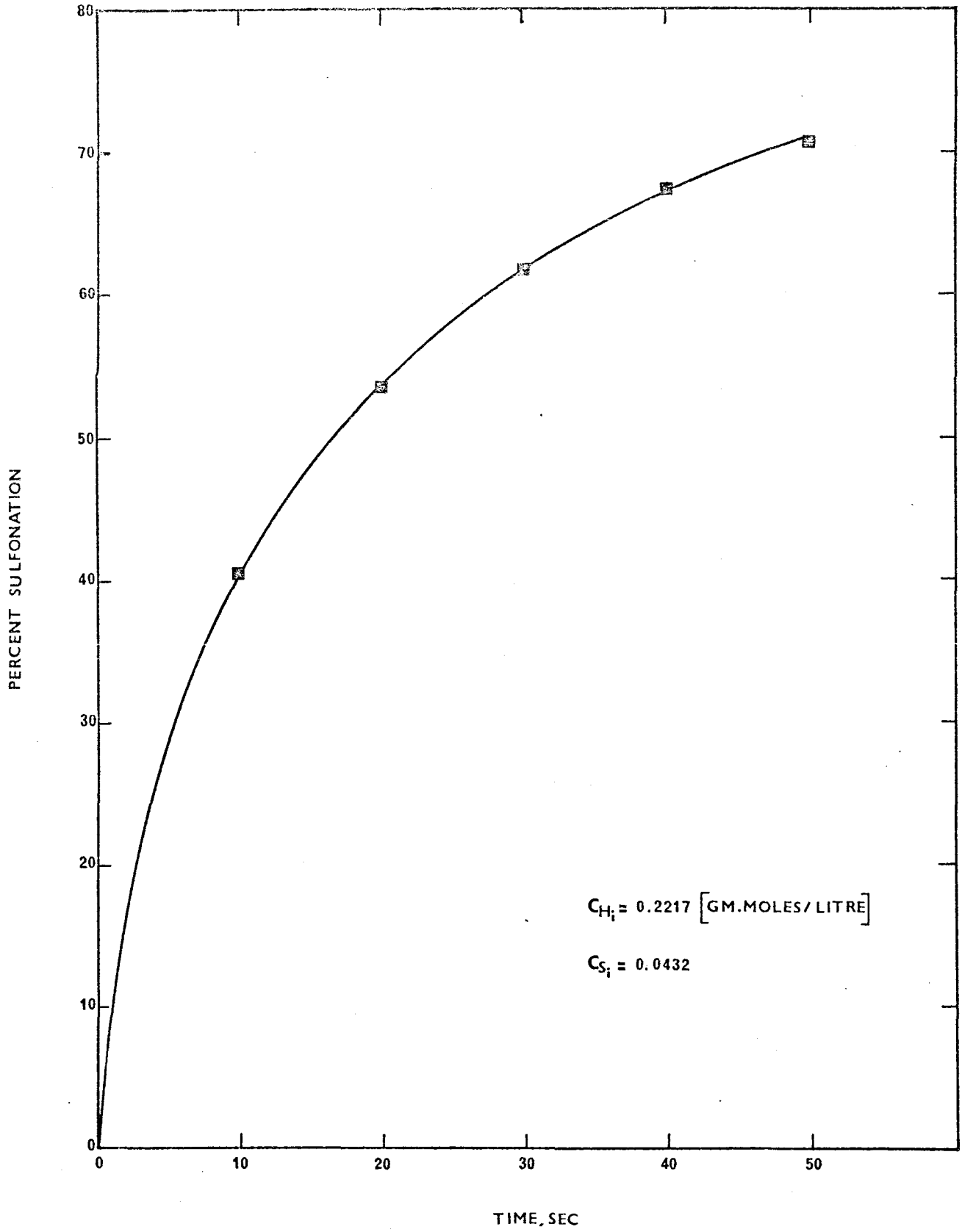


FIG. 21 EXTENT OF SULFONATION

TABLE 7

Summary of Experimental Data

CH_4 = 0.2217 gm.moles/litre

Run no.	Time sec	Titre cm^3	Sulfur-trioxide reacted gm. moles/litre	Sulfur-trioxide present gm. moles/litre
1 A	0	1.250	0.0	0.03700
B	10	0.984	0.01570	0.02130
C	20	0.930	0.01900	0.01800
D	30	0.855	0.02350	0.01350
E	40	0.805	0.02650	0.01050
2 A	0	9.900	0.0	0.06530
B	10	8.170	0.02283	0.04247
C	20	7.820	0.02740	0.03790
D	30	7.920	0.02525	0.04005
E	40	7.700	0.02910	0.03620
3 A	0	8.800	0.0	0.06000
B	10	7.100	0.02320	0.03680
C	20	6.600	0.03000	0.03000
D	30	6.420	0.03249	0.02751
E	40	6.490	0.03140	0.02860
4 A	0	5.700	0.0	0.04700
B	10	4.530	0.01927	0.02773
C	20	4.200	0.02474	0.02226
D	30	4.020	0.02782	0.01918
E	40	3.850	0.03050	0.01650
F	50	3.800	0.03130	0.01570
5 A	0	7.400	0.0	0.06100
B	10	5.820	0.02760	0.03340
C	20	5.220	0.03600	0.02500
D	30	4.900	0.04122	0.01978
E	40	4.600	0.04610	0.01490
F	50	4.500	0.04780	0.01320
6 A	0	6.550	0.0	0.04320
B	10	5.225	0.01750	0.02570
C	20	4.800	0.02302	0.02018
D	30	4.900	0.02670	0.01650
E	40	4.600	0.02920	0.01400
F	50	4.230	0.03060	0.01260

TABLE 8

Summary of Experimental Data

C_{S_i} = 0.04 gm. moles/litre

Run no.	Time sec	Titre cm^3	Dodecylbenzene conc.-initial gm.moles/litre	Sulfur-trioxide reacted %
7 A	0	6.000	0.120	0.00
B	10	4.330		55.60
C	20	4.300		56.66
D	30	3.980		67.25
E	40	3.900		70.00
8 A	0	7.350	0.100	0.00
B	10	5.580		48.80
C	20	5.000		65.00
D	30	4.600		74.93
E	40	4.450		80.00
9 A	0	6.000	0.080	0.00
B	10	4.830		39.00
C	20	4.500		50.00
D	30	4.074		64.20
E	40	3.775		74.16
10 A	0	6.000	0.090	0.00
B	10	4.310		56.40
C	20	4.240		58.70
D	30	3.900		70.00
E	40	3.700		76.66
11 A	0	4.840	0.115	0.00
B	10	3.854		40.60
C	20	3.700		49.17
D	30	3.350		61.57
E	40	3.100		70.75
12 A	0	4.840	0.085	0.00
B	10	3.740		45.50
C	20	3.390		60.00
D	30	3.000		76.63
E	40	2.900		80.16

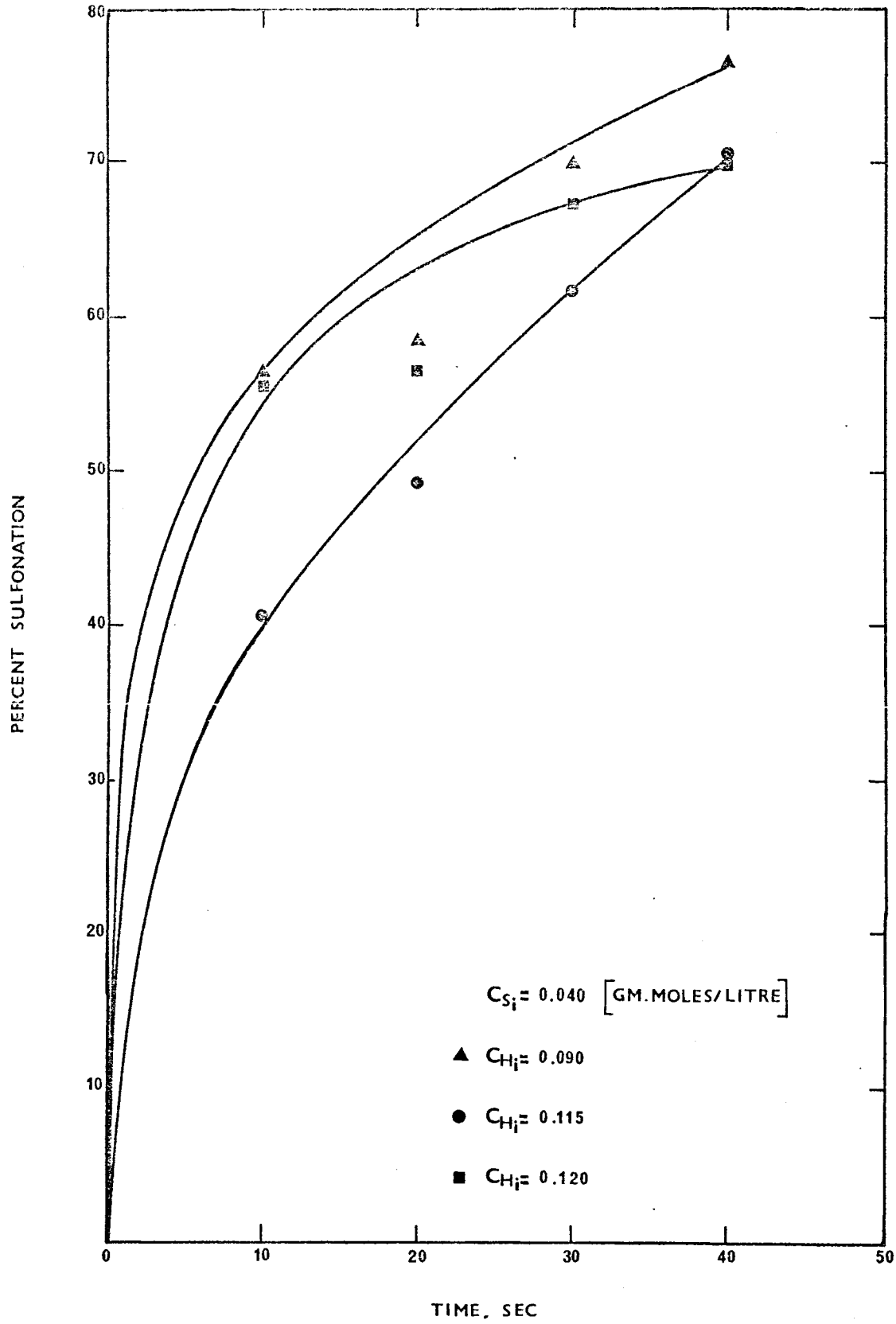


FIG. 22 EXTENT OF SULFONATION

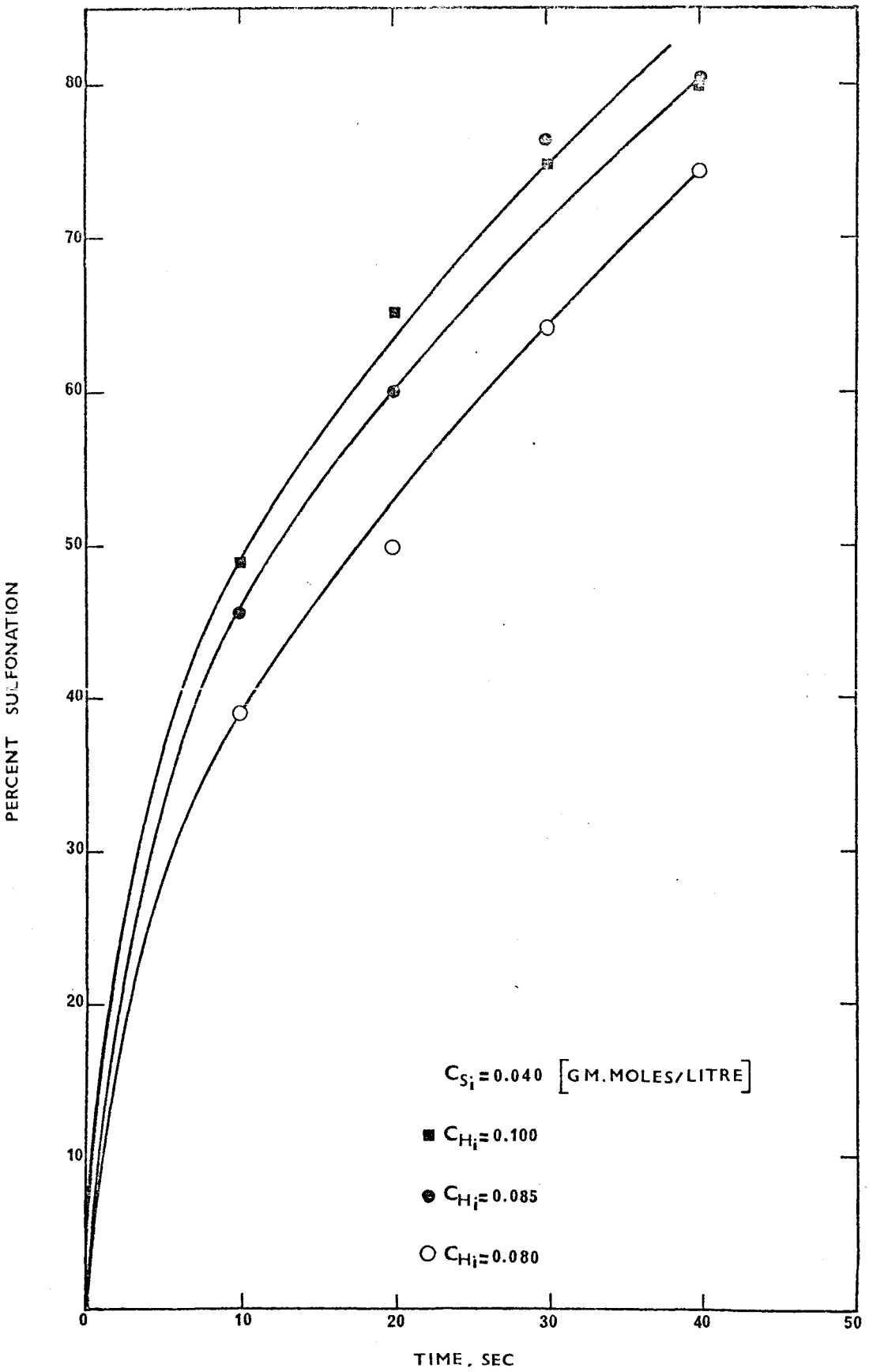


FIG. 23 EXTENT OF SULFONATION

TABLE 9

Summary of Experimental Data

C_{S_1} = 0.04 gm. moles/litre

Run no.	Time sec	Titre cm^3	Sulfur-trioxide reacted gm. moles/litre	Dodecylbenzene present gm.moles/litre
7 A	0	6.000	0.0	0.12000
B	10	4.330	0.02225	0.09775
C	20	4.300	0.02265	0.09735
D	30	3.980	0.02690	0.09310
E	40	3.900	0.02800	0.09200
8 A	0	7.350	0.0	0.10000
B	10	5.580	0.01953	0.08047
C	20	5.000	0.02600	0.07400
D	30	4.600	0.03000	0.07000
E	40	4.450	0.03200	0.06800
9 A	0	6.000	0.0	0.08000
B	10	4.830	0.01560	0.06440
C	20	4.500	0.02000	0.06000
D	30	4.074	0.02567	0.05433
E	40	3.770	0.02965	0.05035
10 A	0	6.000	0.0	0.09000
B	10	4.310	0.02254	0.07746
C	20	4.240	0.02350	0.06650
D	30	3.900	0.02800	0.06200
E	40	3.700	0.03060	0.05940
11 A	0	4.840	0.0	0.11500
B	10	3.858	0.01625	0.09775
C	20	3.700	0.01965	0.09535
D	30	3.350	0.02464	0.09036
E	40	3.100	0.02830	0.08670
12 A	0	4.840	0.0	0.08500
B	10	3.740	0.01820	0.06680
C	20	3.390	0.02400	0.06100
D	30	3.000	0.03065	0.05435
E	40	2.900	0.03210	0.05290

TABLE 10

Logarithmic Variation of Sulfur-trioxide conc. with Time

C_{H_i} = 0.2217 gm.moles/litre

Run no.	Time sec	$\log C_s$
1 A	0	-1.4318
B	10	-1.6700
C	20	-1.7447
D	30	-1.8697
E	40	-1.9788
2 A	0	-1.1851
B	10	-1.3720
C	20	-1.4242
D	30	-1.3979
E	40	-1.4413
3 A	0	-1.2218
B	10	-1.4340
C	20	-1.5216
D	30	-1.5560
E	40	-1.5606
4 A	0	-1.3279
B	10	-1.5509
C	20	-1.6942
D	30	-1.7171
E	40	-1.7825
F	50	-1.8069
5 A	0	-1.2147
B	10	-1.4760
C	20	-1.6021
D	30	-1.7038
E	40	-1.8285
F	50	-1.8794
6 A	0	-1.3645
B	10	-1.5906
C	20	-1.6988
D	30	-1.7825
E	40	-1.8639
F	50	-1.9031

TABLE 11

Logarithmic Variation of Dodecylbenzene conc. with Time

C_{S_i} = 0.04 gm.moles/litre

Run no.		Time sec	$\log C_H$
7	A	0	-0.9208
	B	10	-1.0090
	C	20	-1.0119
	D	30	-1.0410
	E	40	-1.0362
8	A	0	-1.0000
	B	10	-1.0935
	C	20	-1.1308
	D	30	-1.1549
	E	40	-1.1656
9	A	0	-1.0969
	B	10	-1.1906
	C	20	-1.2218
	D	30	-1.2650
	E	40	-1.2984
10	A	0	-1.0458
	B	10	-1.1401
	C	20	-1.1772
	D	30	-1.2076
	E	40	-1.2269
11	A	0	-0.9393
	B	10	-1.0100
	C	20	-1.0209
	D	30	-1.0443
	E	40	-1.0620
12	A	0	-1.0706
	B	10	-1.1749
	C	20	-1.2147
	D	30	-1.2636
	E	40	-1.2765

TABLE 12

Summary of Results

Calculation of Initial Reaction Rates

Run no.	dlogC_i/dT	Initial conc.	dC_i/dT	log(dC_i/dT)
		C_{Si}		
1	0.1700	0.0370	0.00637	-2.1959
2	0.2570	0.0653	0.01682	-1.7747
3	0.2200	0.0600	0.01320	-1.8794
4	0.1900	0.0470	0.00894	-2.0487
5	0.2300	0.0610	0.01400	-1.8539
6	0.1500	0.0432	0.00648	-2.1884
		C_{Hi}		
7	0.0498	0.1200	0.00598	-2.2232
8	0.0540	0.1000	0.00540	-2.2676
9	0.0580	0.0800	0.00464	-2.3335
10	0.0528	0.0900	0.00475	-2.3233
11	0.0484	0.1150	0.00557	-2.2541
12	0.0586	0.0850	0.00498	-2.3028

TABLE 13

Calculation of Linear Multiple Correlation Co-efficient

$\log(\text{rate})_{ave} = -2.1373$

Run no.	$\log R_{exp}$	$\log R_{cal}$	$\log R_{exp} - \log R_{cal}$ d	$\log R_{exp} - \log R_{ave}$ x
1	-2.1959	-2.1977	+0.0018	-0.0583
2	-1.7747	-1.7574	-0.0173	+0.3624
3	-1.8794	-1.8223	-0.0571	+0.2577
4	-2.0487	-2.0124	-0.0363	+0.0884
5	-1.8539	-1.8089	-0.0450	+0.2832
6	-2.1884	-2.0767	-0.1117	-0.0513
7	-2.2232	-2.2873	+0.0641	-0.0861
8	-2.2676	-2.3319	+0.0643	-0.1305
9	-2.3335	-2.3864	+0.0529	-0.1964
10	-2.3233	-2.3576	+0.0436	-0.1862
11	-2.2541	-2.2977	+0.0436	-0.1170
12	-2.3028	-2.3716	+0.0688	-0.1657

$\Sigma d^2 = 0.03823512$

$\Sigma x^2 = 0.43068133$

Now, $r^2 = 1 - \Sigma d^2/\Sigma x^2$ (14)

$= 1 - 0.088778$

$= 0.911222$

$\therefore r = 0.9545$

where, r= linear multiple correlation co-efficient, which is, a fraction of total variance of logarithmic initial reaction rate contributed by its regression upon the variables log(hydrocarbon conc.) and log(sulfur-trioxide conc.).

TABLE 14

Calculation of Linear Multiple Correlation Co-efficient

$Rate_{ave} = 0.0072913$

Run no.	$Rate_{exp}$	$Rate_{cal}$	$R_{exp}-R_{cal}$ d	$R_{exp}-R_{ave}$ x
1	0.00637	0.006345	-0.000250	+0.00092
2	0.01632	0.017480	+0.000660	-0.00953
3	0.01320	0.015050	+0.001850	-0.00591
4	0.00894	0.009728	+0.000788	-0.00165
5	0.01400	0.015520	+0.001520	-0.00671
6	0.00648	0.008380	+0.001900	+0.00081
7	0.00598	0.005160	-0.000820	+0.00131
8	0.00540	0.004650	-0.000750	+0.00189
9	0.00464	0.004108	-0.000532	+0.00265
10	0.00475	0.004389	-0.000361	+0.00254
11	0.00557	0.005039	-0.000531	+0.00172
12	0.00498	0.004250	-0.000730	+0.00231

$\Sigma d^2 = 0.000012921144$

$\Sigma x^2 = 0.000202054900$

Now, $r^2 = 1 - \Sigma d^2/\Sigma x^2$ (14)

$= 1 - 0.063948$

$= 0.936052$

$\therefore r = 0.9674$

Where, r = linear multiple correlation co-efficient, which is, a fraction of total variance of initial reaction rate contributed by its regression upon the variables hydrocarbon concentration and sulfur-trioxide concentration.

VITA AUCTORIS

1946 Born in Calcutta, W.Bengal, India on July 16.

1968 Received the Bachelor of Technology (Honours) degree in Chemical Engineering from the Indian Institute of Technology, Kharagpur, W.Bengal, India in the month of May.

1968 Accepted in September into the Graduate School of the University of Windsor, Windsor, Ontario, Canada as a candidate for the degree of Master of Applied Science in Chemical Engineering.